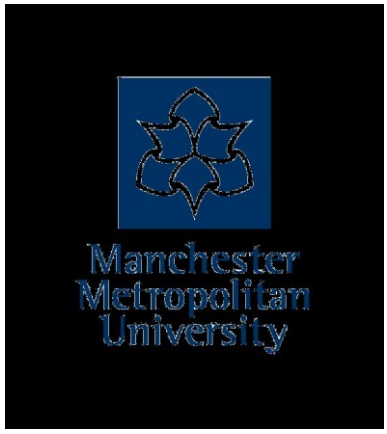

Analysis and Control of Emissions arising from Stabilised Polypropylene and the Incorporated Additives

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A thesis submitted in the partial fulfilment of the requirement of the Manchester Metropolitan University for the degree of Doctor of Philosophy

School of Biology, Chemistry and Health Sciences

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To

Keith, Khalil, and my Parents

Declaration

This is to certify that the material contained in this thesis has not been accepted in substance for any other degree and is not currently submitted in candidature for any other academic award.

Aneela Arshad

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SUMMARY

Thermo-oxidative degradation of polypropylene (PP) stabilised with a range of antioxidants of commercial applications is investigated by a simultaneous analysis of the chemical changes in the slid polymer mass, both in solid and molten state, as well as in the headspace of the samples as they degraded. Provided the thermo-oxidative degradation of un-stabilised PP has already been discussed in literature in breadth, the current work focuses on the degradation of the polymer stabilised with a range of antioxidants of commercial importance. Both the degradation of the polymer and the non-polymeric constituents i.e. the antioxidants and other additives, is critically evaluated and discussed in the context of contemporary research. The antioxidants targeted in the current study belong to a range of families of stabilisers with different structural features and stabilisation mechanisms, and were mixed to give fifteen formulations of different composition. A systematic way of mixing was adopted so that the experimental observations could be interpreted in more systematic and simpler way, and maximum possible information could be extracted from them.

Experimental analysis of thermo-oxidative degradation was conducted by analysing structural changes inside the solid polymeric mass, both in solid and molten state, by attenuated total reflectance infrared (ATR-IR) and chemiluminescence (CL) spectroscopic methods, respectively. The emissions generated by the aged polymeric formulations were carefully and thoroughly analysed by chromatographic-mas-spectrometric (GC-MS) methods. The GC-MS and ATR-IR analysis has been conducted at 90°C, 120°C and 150°C, over multiple ageing periods, in presence of air. It is important to mention that while the spectroscopic methods were comparatively simpler, it took an extensive method development work for the GC-MS work, especially on the account of pre-analytical extraction and trapping required for the emissions. The results of method development stage proved useful in assessing the potential of various sampling techniques i.e. static headspace extraction (SHE), solid-phase micro-phase extraction (SPME), thermal desorption (TD) and micro-scale-sealed-vessel extraction (MSSV), eventually finding SPME and MSSV as more appropriate methods for the actual analytical testing work for the current project. Through a comparison of multiple analytical techniques, it has been emphasised that conventional and so-called standard testing methods (SHS and TA) are surpassed by the methods not so commonly used in the field of polymer analysis (SPME and MSSV).

It is interesting that, despite the variations in their working principles and the physical states of the samples used in each individual method, a significant correlation was found among the results of the three experimental methods (ATR-IR and CL spectroscopic, and GC-MS methods). The correlation became more pronounced for the emissions at 150°C and the CL results of the samples. In general, the emissions measured by GC-MS analysis proved to a more sensitive method to study degradation than the conventionally used spectroscopic methods. Addition, the emissions data was more value-added both in qualitative and quantitative aspects, and was more reflective of the changes in the degradation/experimental conditions i.e. time and temperature, and composition of the samples i.e. stabilisation packages.

A review of the spectroscopic and chromatographic data revealed that thermo-oxidative degradation chemistry of PP changes significantly in response to any changes in the stabilisation packages. The changes are so significant that they tend to limit the relevance of important established kinetic and mechanistic explanations (proposed for the degradation behaviour of un-stabilised form of PP) for the polymer in its stabilised form. Among the emissions, a significantly low proportion of the functionalities characteristic of tertiary alkyl radical oxidation pathways, and substantially high proportion of the compounds commonly associated with oxidation chemistry that begins with primary and secondary alkyl radicals, for example, does not support the so-called tertiary carbon chemistry that tends to prevail PP degradation literature. The apparently low representation of the methine among the products in PP emissions can be due to their preferred suppression by stabiliser. Similarly, almost negligible presence of alcohols among the emissions as well as in the corresponding IR spectra of the degraded polymer, reduced the role of the homolytic hydro-peroxide decomposition. It is important because, although significantly undermined for thermo-oxidative degradation in PP, homolytic decomposition of hydroperoxides still forms an important part of many kinetic and mechanistic schemes associated with PP degradation. Further, it has been observed that a range of compounds that have widely been reported and discussed in the context of PP degradation form either only a minor proportion of the total emissions from the stabilised PP formulations, or are too negligible to be detected even with a sensitive method like SPME-GC-MS. It has been observed that, the hydrocarbons that form the major part of the PP emissions (70-90 % of the total emissions, in general) have been previously under-represented in discussions on degradation of PP. A general trend of higher hydrocarbon emissions accompanied with relatively lower oxidation products has been observed across all formulations suggesting a relation between the two groups of compounds. Such a trend has also been observed to bear a correlation with the stabilisers used in a formulation, e.g. higher hydrocarbon and low oxidation content

were characteristic of the formulations containing the phosphite-type antioxidant, while the reverse has been observed for the formulations with hydroxylamine replacing the phosphite.

In stabilised PP, unlike the un-stabilised form of the polymer, any non-polymeric components of the formulations i.e. antioxidants/additives, catalytic residues and contaminants etc., initiate a parallel regime of degradation and stabilisation chemistry. The current study has revealed interesting synergist and antagonistic relations between a range of antioxidants from commonly used families of stabilisers, e.g. phosphites, hydroxylamine, hindered phenols, thioesters, light stabilisers and natural antioxidants etc. Such interactions, unlike the common understanding in polymer research community, were specific to the antioxidant families as well as individual antioxidants, e.g. while phosphite showed a general synergy for the hindered phenols, the interaction of the individual thioesters varied with the type of an individual hindered phenol. The effect of physical factors, e.g. thermal degradation of the parent antioxidant structure, on the stabilisation capacity of the antioxidants has been also been demonstrated through the analysis of the antioxidant degradation products.

In short, the role of emissions, in conjunction with the conventional spectroscopic methods of analysis, has been appreciated as an enriched way to study early stages of PP degradation in the stabilised form of the polymer. Previously used to corroborate the macromolecular degradation mechanisms and fit into the existing theories, in the current study the emissions data has indeed been at the basis of the key questions related to PP degradation chemistry. It has also effectively been used as a framework to design more logical and fulfilling research targets and recommendations for any further works on the subject.

Acronyms/Abbreviations

ATR-IR: Attenuated total reflectance infrared

CA: Carboxen

CaSt: Calcium stearate

CI: Carbonyl index

CIEEL: Chemically Induced Electron Exchange Luminescence

CL: Chemiluminescence

CLMS: Closed-Loop Mechanistic Scheme

DLTDP: Dilauryl thiodipropionate

DSTDP: Distearyl thiodipropionate

dSPME: Dynamic Solid-Phase Micro-Extraction

DVB: Divinyl benzene

EPR: Electron Paramagnetic Resonance

FTIR: Fourier Transformer Infrared

GA-80: 3, 9-Bis [2-[3-(3-tert-butyl-4-hydroxy-5-methylphenyl) propionyloxy]-1, 1-dimethylethyl] - 2, 4, 8, 10-tetraoxaspiro, undecane

GC-FID: Gas Chromatography Flame Ionization Detector

GC-MS: Gas Chromatography Mass Spectrometry

IS: Internal standard

LMWCs: Low Molecular Weight Compounds

MSSV: Micro-Scale Sealed-Vessel

ODE 23 and 45: Ordinary Differential Equation Solver 23 and 45

OIT: Oxidative Induction Time

-oxy radicals: Alkoxy and peroxy radicals

PA fibre: Polyacrylate fibre

PDMS: Polydimethylsiloxane

PE: Polyethylene

PFTA: Perfluorotetradecanoic acid

PP: Polypropylene

SFE: Solvent-free extraction

SHE: Static headspace extraction

SIM: Selective Ion Monitoring

SN1680: Tris (2, 4-di-tert-butylphenyl) phosphite

SN1010: Pentaerythritol tetrakis (3-(3, 5-di-tert-butyl-4hydroxyphenyl) propionate

SN4120: Pentaerythrityl thiodipropionate

SVOCs: Semi-volatile organic compounds

sSPME: Static Solid-Phase Micro-Extraction

TD: Thermal Desorption

Th: Tesla

TIC: Total Ion Chromatogram

VDA-278: Vehicle Development Authority method 278

VOCs: Volatile Organic Compounds

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CHAPTER: 1. INTRODUCTION

1.1. Research background

Versatile physiochemical and engineering properties, low cost and easily accessible raw material makes polypropylene (PP) an important material for use in industries like automotive, electronics, packaging, medical devices and small appliances of everyday use. Development of better polymerization methods, compounding techniques, and stabilisation packages has extended its use from a material for everyday applications to a speciality material. The main drawback of PP as a material is its propensity to degradation. A variety of intrinsic (extensive branching in the polymeric chains, and catalytic and residual impurities) and extrinsic factors (heat, light, oxygen, and pressure) can trigger various types of polymer degradation reactions that can lead to a serious deterioration of physiochemical properties of the polymer and, if left unabated, to an eventual failure [1-3].

Realising its importance, the studies on the degradation of PP started even before the polymer was commercially introduced. The early investigations conducted to study thermo-oxidative degradation used small molecular weight systems, e.g. ethyl linoleate, and revealed very useful information about degradation of hydrocarbons. The mechanistic and kinetic schemes that were proposed almost a century ago are still considered main explanations of the oxidation chemistry. The limitations of such theories to explain degradation of polymeric systems, especially under service life conditions, was realised soon after and attempts have been made by polymer researchers to resolve them ever since [4-7]. Over time, development of better analytical instrumentation made it possible to investigate PP degradation directly by analysing physiochemical changes in the polymer in response to multiple intrinsic and extrinsic factors, e.g. the effect of temperature, oxygen, impurities, structural defects and the structure of the polymer itself [7-9]. Analysis of the emissions from oxidised polymer was adopted with the development of more sensitive instruments, capable of analysing trace-level of compounds of complex chemical nature, e.g. GC-MS. Macromolecular chemistry, in conjunction with analysis of low molecular weight compounds evolved during the oxidation of a polymer, forms an important part of the complex jigsaw of polymer degradation chemistry. Further, the analysis of the emissions has been found useful to assess any toxicological concerns associated with the material [3, 10, 11]. It appears that simultaneous analysis of the degradation process inside a solid polymeric matrix and of any subsequently generated emissions is more likely to lead to a better understanding of the degradation, and is the subject of the current study.

An all-inclusive kinetic model has been the goal of polymer researchers during past two decades. During this period the complex network of polymer degradation reactions has in reality been replaced by the so-called prevalent mechanistic approach/pathways. An important example of this approach is the 'The Closed-Loop Mechanistic Scheme (CLMS). Proposed in 1990s, CLMS is based on reducing an all-inclusive mechanistic scheme to key reactions of vital importance in the cycle. Identification of the rate-determining steps in a chain of multiple reactions is the heart of this approach. Extending this treatment to the entire degradation cycle is expected to give a reliable blue print for the degradation process [12]. Despite its inherent limitations, the approach has received wide acclaim in the polymer research community, and is appreciated for its simpler nature. Capitalising on the effect of various intrinsic and extrinsic factors, this tactic has been used to develop more specific versions of the generalised degradation models, e.g. kinetic models for photo-oxidative and thermo-oxidative degradation. Although, for the sake of simplicity, the majority of studies tend to consider one-factor at a time, there is also a trend to converge and update the existing single-factor formalisations/models into multifactor simulations [12, 13]. There is a long way to go before a universal model for polyolefin degradation can be developed, one key feature of any such model, should be its ability to simulate service-life conditions of a polymer. In this context, one important factor that needs more attention is the role of additives/stabilisers. For the sake of simplicity in analysis, most of the studies on degradation of PP tend to use the un-stabilised form of the polymer. The literature, especially on the emissions from the stabilised PP formulations, is rather limited [14, 15]. Since the phenomenon of polyolefin degradation, in general, is too wide to be covered under a single study, the current work focuses on thermo-oxidative degradation of PP with stabilisation as the major factor in presence [3, 16].

1.1.1. Aims of study

The aim of the current project is to investigate thermo-oxidative degradation in PP stabilised with a range of commercially used antioxidants, and re-evaluate the mechanistic and kinetic models of thermo-oxidative degradation with improved knowledge of the role of emissions.

1.2. Polypropylene

PP is the most important thermoplastic after polyethylene (PE). Initially discovered in the second half of the 19th century, the polymer could only find its way into commercial markets after the Nobel Prize winning discovery of Zeigler-Natta catalysts, by Karl Zeigler in 1955. Soon after its commercialization, PP went through a phenomenal growth that reached its maximum during 1960-1970, and its growth is still well sustained. The success of PP as a material owes itself to its versatile physiochemical properties (Table: 1.1), easy availability of raw material, and development in polymerization and processing methods.

Table: 1. 1. Physical properties of Polypropylene.

Property	**Value**
Density	0.90-0.91 g cm^{-3}
Crystallinity	45-55 %
Melting point	160-170 °C
Tensile strength	4500 psi
Molecular weight	220,000 -700,000 g mol^{-1}
Glass transition temperature	0 °C

Synthesised by polymerization of propene, a by-product of the petroleum industry, PP is found in three different isomeric forms i.e. syndiotactic, atactic and isotactic. Although the only difference in the chemical structure of the three isomers is the relative position of the pendant methyl group, this apparently small difference significantly affects physiochemical properties and eventual applications of the PP isomers. Syndiotactic and isotactic isomers, for example, are the main resins used in the PP industry, while atactic PP is only used as an adhesive. Although the Zeigler–Natta catalyst still accounts for majority of the PP synthesised across the globe, new generations of catalysts are being introduced to achieve better control over regio-selectivity and purity of the polymer [3, 17, 18].

Over the years, development of additives (fillers, pigments and antioxidants) as well as its copolymerisation of PP with other polymer has made the polymer an omnipresent material with applications ranging from an everyday resin to the material used in speciality equipment. Automotive and medical equipment, textile, packaging, consumer products and construction material for building interiors are only few on a long list of its areas of applications. While the polymer has been improved to cope with the competitive market trends, it degradation is still a problem, and is subject of a wide area of research [2, 16, 18, 19].

1.3. Chemistry of thermo-oxidative degradation of PP

PP undergoes continuous degradation throughout its life cycle. The number of agents that can trigger degradation are numerous and so are the subsequent degradation pathways. Although, thermo-oxidative degradation predominates the processing stages and service life of PP, various other types of degradation pathways, e.g. photo degradation and mechanical scission etc., are simultaneously in operation to varying extent at any given stage of the life cycle of the polymer [20-24]. The complicated chemistry that could arise from such a situation has apparently been tackled by the assumption that, except for the initiation stages, the overall chemistry of various types of degradation processes is similar. A mechanistic or kinetic model therefore, with some adjustments to account for the initiation stages i.e. the nature of the initiating species and the rate-determining step, can be used to describe various types of degradation processes. Photo-oxidative degradation, for example, differs from thermo-oxidative degradation due to the carbonyls that absorb the light resulting in Norrish Type I and Norrish Type II processes [12, 25-27]. Due to its relevance to the tile of the current project, for now, only the chemistry of thermo-oxidative degradation of PP is discussed in this section.

Thermo-oxidative degradation, in general, is the result of thermal scission of the polymeric chains and their oxidation. In an inert environment, thermal degradation has been described as random scission of a polymeric chain into fragments that undergo β-scission leading to the formation of small alkyl and vinyl compounds. The alkyl radicals formed by random scission can also undergo inter- and intra-molecular hydrogen transfer.

The intramolecular hydrogen transfer, also known as the back-biting reaction, can occur up to the fifth carbon of polymeric chain, forming isomers of primary radicals that are relatively more

stable, e.g. secondary and tertiary alkyl radicals. Unlike intramolecular hydrogen transfer, the intermolecular hydrogen transfer is more than a mere isomerisation process; it is in fact considered to be a main reaction involved in the propagation of thermal degradation. Post β-scission intermolecular hydrogen transfer also form vinyl groups in the secondary alkyl radicals, and vinyldene and vinylene groups in the tertiary alkyl radicals [3, 27]. Unlike thermal degradation, the chemistry of oxidation of materials is a very complicated process.

As early as the first half of the 19th century, oxidation of material was considered to involve oxygen and hydrogen peroxide. Further work showed hydroperoxides among the primary intermediate products of oxidation in hydrocarbon-based systems [28]. The formation of hydroperoxides and their role in oxidation of hydrocarbons was explained by free radical mechanisms of auto-acceleratory limited to cover all aspects of oxidation in a polymer undergoing a complex life-cycle [4-6, 20, 29-31]. However, despite its simplistic nature and apparent limitations, the auto-oxidative mechanism of polyolefin degradation served as the foundation of the studies that followed decades of research, and is still considered the foundation stone of degradation and stabilisation of hydrocarbons. In thermo-oxidative degradation, thermal and oxidative processes occur simultaneously. At high temperature the activation energy of various oxidation reactions changes, often reducing in magnitude it leads to increase in oxidation of the material [20, 32].

In all established explanations and mechanisms, thermo-oxidative degradation is a cyclic process of self-propagating character. Although it is hard to draw a physical boundary between the various stages or steps of the process, for the sake of simplicity, the cycle is typically divided into initiation, propagation, and termination stages. Each stage is characterised by a set of chemical reactions and subsequently formed products, which are described in detail in the sections that follow.

Initiation

$RH \longrightarrow R^{\bullet}$ 1

$RH + O_2 \longrightarrow R^{\bullet} + {}^{\bullet}OOH$ 2

Catalyst residues $\longrightarrow$ Free radicals.....3

Propagation

$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$ (peroxy radical) 4

$ROO^{\bullet} + RH \longrightarrow ROOH$ (hydroperoxide).....5

Branching

$ROOH \longrightarrow RO^{\bullet}$ (alkoxy radicals) $+ {}^{\bullet}OH$ (hydroxy radical)....6

$RO^{\bullet} + RH \longrightarrow ROH$ (alcohol) $+ R^{\bullet}$.....7

$2ROO \longrightarrow ROO^{\bullet} + RO^{\bullet} + H_2O$.....8

$ROOH + RH \longrightarrow RO^{\bullet} + R^{\bullet} + H_2O$.....9

$HO^{\bullet} + RH \longrightarrow H_2O + R^{\bullet}$.....10

Termination

$ROO^{\bullet} + ROO^{\bullet} \longrightarrow ROOR + O_2$.....11

$ROO^{\bullet} + ROO^{\bullet}$ (tertiary) $\longrightarrow RO^{\bullet} + RO^{\bullet} + O_2$.....12

$ROO^{\bullet} + ROO^{\bullet}$ (primary/secondary) $\longrightarrow ROH + C{=}O + O_2$.....13

$R^{\bullet} + ROO^{\bullet} \longrightarrow ROOR$ 14

$R^{\bullet} + R^{\bullet} \longrightarrow R\text{-}R$ 15

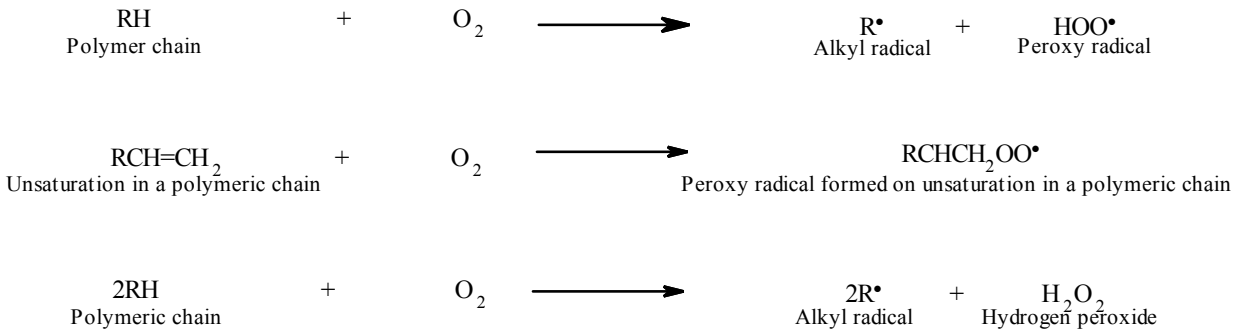
Scheme: 1.1. Auto-oxidative degradation of polyolefin. (Symbols: R stands for an alkyl chain/fragment or group) [3].

1.3.1. Initiation

Initiation is the first stage of the auto-acceleratory cycle of thermo-oxidative degradation in polyolefins. It triggers in response to multiple factors of extrinsic and intrinsic nature. The ultimate output of the initiation can be described as generation of radicals that can serve as feedstock into the subsequent stages i.e. propagation, of the degradation cycle. Despite the controversy that surrounds the explanation behind their formation, alkyl radicals have continuously been considered as the key initiating species for thermo-oxidative degradation in polyolefins. During thermo-oxidative degradation alkyl radicals are formed by random chain scission as well as hydrogen abstraction from a polymeric chain. While the former is an accepted corollary to the mechanical shear and high processing temperature, hydrogen abstraction is generally initiated by species that have affinity for hydrogen, e.g. oxygen, polymer chain unsaturation etc. Formation of alkyl radicals as initiation species in polyolefin degradation has been a controversial topic due to endothermic nature of the reaction, and has been attempted to be explained by several explanations. One such explanation is the widely known role so-called initiating species, e.g. structural defects and impurities inside a polymeric matrix. The initiating species can be of extrinsic and intrinsic nature.

The extrinsic agents are non-polymeric in origin mainly including residual catalytic impurities, species formed by reactions of oxygen with the impurities, and structural defects in the polymer. The intrinsic factors/agents on the other hand, have their origin inside the polymeric chain and include hydroperoxides (formed by oxidation reactions along a polymeric chain) as the key example [33].

Incorporation of oxygen into a polymeric chain



Scheme: 1.2. Alkyl radical formation during initiation of polyolefin degradation [37, 38].

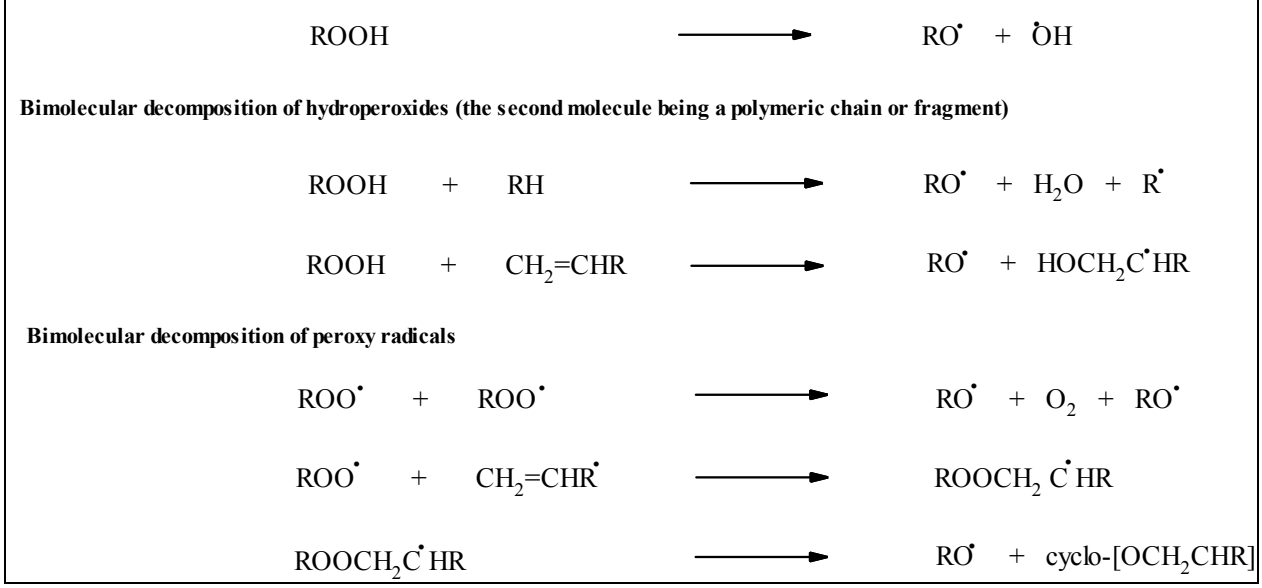
To begin with the initiators of extrinsic nature: residual catalytic impurities have been reported to play an important role in initiation of auto-oxidative degradation cycle. The catalytic impurities are mainly transition metal-based salts. Depending on their active concentration, oxido-reductive potential, and the nature of the attached ligands, they are reported to function both as promoters and as inhibitors of thermo-oxidative degradation. Their role as inhibitors has been associated with their ability to degrade hydroperoxides and scavenge the macro-alkyl radicals in a polymeric matrix. The role of transition metals as promoters of oxidative degradation has been described in many studies but devoid of explanation on the underlying chemistry [24, 34, 35]. Other than the catalytic impurities, environmental oxygen that diffuses into the amorphous region of the semi-crystalline polymeric matrix of polyolefin is also known for its direct and indirect role in the formation of alkyl radicals. In the indirect way: oxygen interacts with unsaturation and aromatic impurities in polymeric chains, generating ethylenic-hydroperoxide complexes of various types. An ethylenic hydroperoxides, once formed along a polymeric chain, promotes hydrogen abstraction from the carbon centres in its vicinity. The direct role of oxygen in the formation of alkyl radicals has been explained through three different mechanisms (Scheme: 1.2). The mechanisms have also been proven experimentally [21, 36].

The intrinsic factors that promote formation of alkyl radicals include structural features, e.g. unsaturation and branching along a polymeric chain. The structural defects have higher affinity for oxygen forming a range of oxygen-based free radicals, e.g. alkoxy, peroxy and hydroperoxides etc. (Scheme: 1.2). A diverse combination of oxygen-based free radicals, e.g. alkoxy etc. has been reported to be present in the polyolefin matrix as early as pre-processing stages of polymer life-cycle. The relative concentration of the alkoxy and peroxy radicals during initiation, however is considered too low to cause any substantial impact on the properties of the material. Rather, they are mainly considered for their role in the formation of alkyl radicals by hydrogen abstraction from reactive sites along a polymeric chain. Hydrogen abstraction in a polymeric chain occurs in the order of alpha position to a C=C > benzyl hydrogen > tertiary hydrogen > secondary hydrogen > primary hydrogen. The alkoxy/peroxy radicals of primary and secondary nature, due to their more reactive nature, are faster at hydrogen abstraction than those of tertiary nature. In PP, alkyl radicals are formed in substantially higher proportion than other polyolefins, mainly due to presence of branching in the polymer.

1.3.2. Propagation

The propagation stage of thermo-oxidative degradation can simply be described as continuous consumption and re-generation of free radicals through a series of repeated oxidation and hydrogen abstraction reactions. At the propagation stage, a polymeric matrix is a mixture of various free radicals. Interactions among those radicals define actual chemistry of 'propagation'. Alkyl, alkoxy and peroxy radicals, and hydroperoxides are the key primary chemical species involved in propagation of thermo-oxidative degradation of PP. As the propagation proceeds, however the interactions among the primary populations of free radicals generates a secondary population of free radicals and molecular species. One-way to look into 'propagation' chemistry is to follow the chemistry of the individual free radicals involved in this stage and trace their fate and mutual interactions through the cycle.

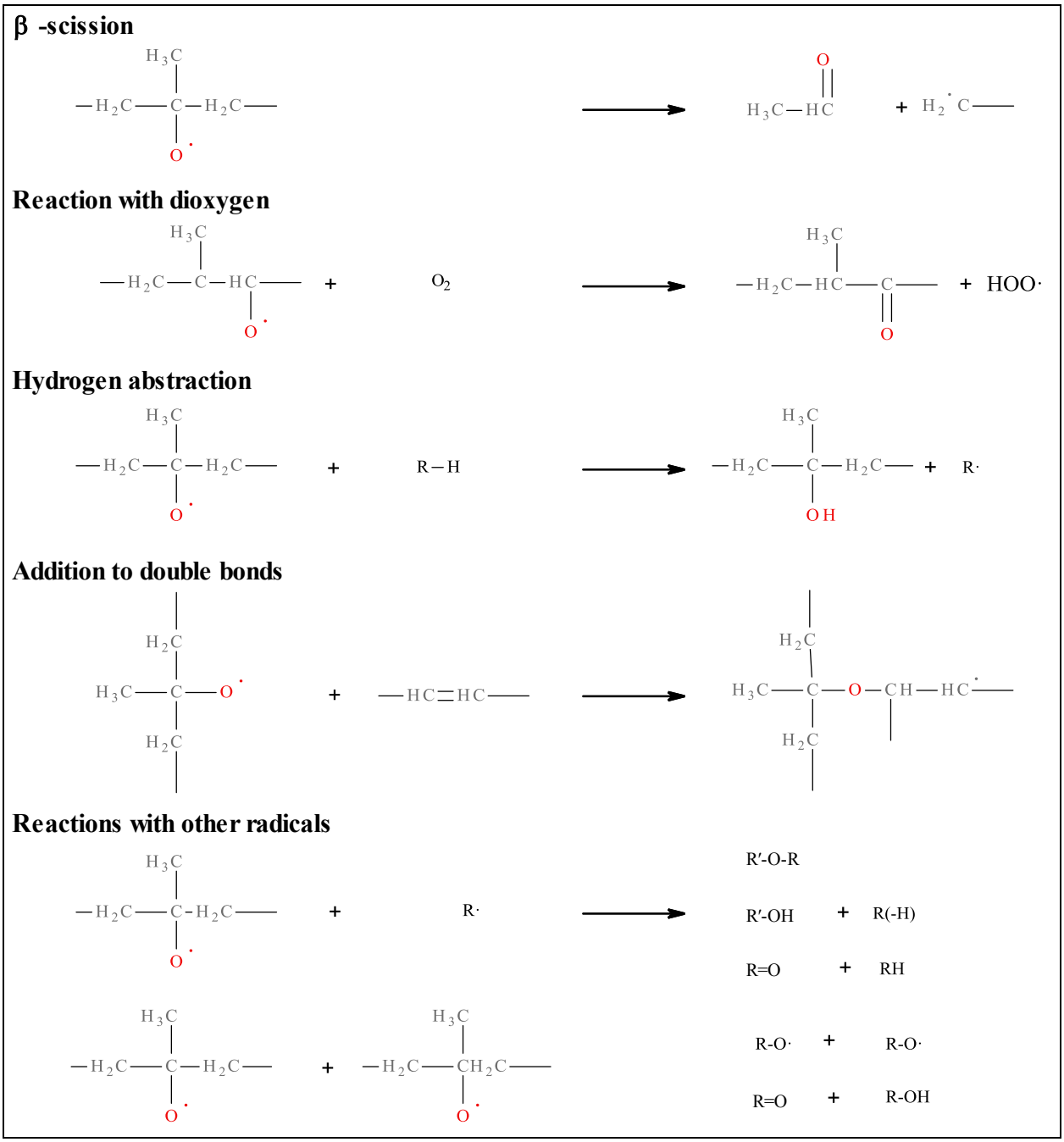
Unimolecular decomposition of hydroperoxides in Polypropylene



Scheme: 1.3. Formation of alkoxy radicals (RO°) during thermo-oxidative degradation of PP matrix [39].

Starting with alkyl radicals, the precursors of most of the other radicals formed at various stages of the thermo-oxidative degradation cycle, one meets with the challenge of ascertaining the reaction behind their formation. Chemically endothermic, they are not thermodynamically favoured unless tempered by the presence of so-called initiators, e.g. oxygen, hydroperoxides, impurities and structural defects in the polymeric chains. The uncertainty in the mechanisms for their formation however, does not seem to undermine the prevalent interest in their role in propagation of auto-oxidative degradation cycle of polyolefin. Once formed, alkyl radicals are readily attacked by oxygen. Consecutive oxidation reactions convert the alkyl radicals into

alkoxy and peroxy radicals. Peroxy radicals, chemically too unstable, are reduced into hydroperoxides after hydrogen abstraction from vulnerable/ reactive sites along the polymeric chain. Hydroperoxides, relatively stable chemical species, are formed through a reaction that not only carries an auto-acceleratory character, but is also slow enough to be used as a rate determining reaction for the propagation phase of thermo-oxidative degradation in polyolefin. The extraordinary role of hydroperoxides in thermo-oxidative degradation chemistry is reviewed in the Section: 1.3.2.1. in detail.



Scheme: 1.4. Chemical reactions of alkoxy radicals in a polyolefin matrix [40-42].

Alkoxy radicals, formed either by direct oxidation of alkyl radicals or through decomposition of hydroperoxides (Scheme: 1.3), undergo various reaction, e.g. β-scission, hydrogen abstraction, addition to a double bond, reaction with di-radical of oxygen (Scheme: 1.4) generating a range of carbonyl species, e.g. ketones, aldehydes and acids. Chemistry of the alkoxy radicals however, is mostly associated with their tertiary form (Scheme: 1.4 and 1.10), as the primary and secondary alkoxy radicals are usually considered too unstable to exist in substantial yield in most of the degradation pathways of degradation cycle [15, 40].

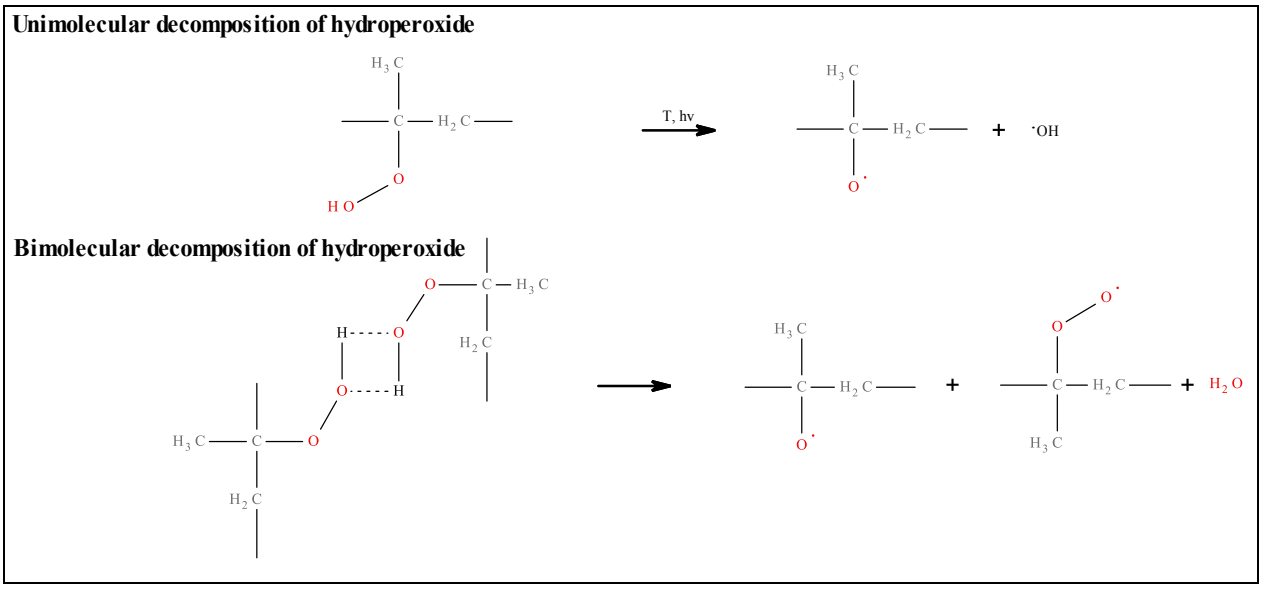
The sequence of reactions described so far is a relatively simpler description of the propagation, and applies mainly to free radicals of tertiary nature. As thermo-oxidative degradation progresses and the free radicals build in their concentration, the chemistry of their interactions becomes more complex and diverse. This stage, characterised by higher rate of degradation, is known as branching phase of the auto-oxidative degradation cycle (Scheme: 1.1.). Unimolecular and bimolecular decomposition of hydroperoxides are considered the key reactions of branching phase. Each of the two types of the reactions generates further radicals affecting subsequent chemistry of the process (Scheme: 1.5).

1.3.2.1. Hydroperoxides as thermo-oxidative degradation intermediates

As described earlier, hydroperoxides are the key species involved in the propagation phase of thermo-oxidative degradation in polyolefin, and are among the primary products of thermo-oxidative degradation cycle. They are formed by isomerisation or reduction of peroxy radicals. Under mild oxidation conditions i.e. below 400 K, hydroperoxides have been reported to account for most of the oxygen consumed by an oxidised polymer, and are the source of most of the degradation products of volatile and semi-volatile nature evolved by the polymer. Hydroperoxides are relatively more stable than other oxygenated radicals and molecular species, and are formed by a relatively slow chemical reactions, making them more important in studies on polymer degradation.

The main role of hydroperoxides in thermo-oxidative degradation is related to their decomposition and the chemistry that is initiated by the decomposition products (Scheme: 1.5 and 1.6). In the early works hydroperoxides decomposition was described as homolytic cleavage of low dissociation energy (150 kJ mol^{-1}) O-O bond generating alkoxy and hydroxyl species

(Scheme: 1.5). The products of homolytic cleavage i.e. alkoxy and hydroxyl radicals, are too unstable and almost instantly converted into secondary species.



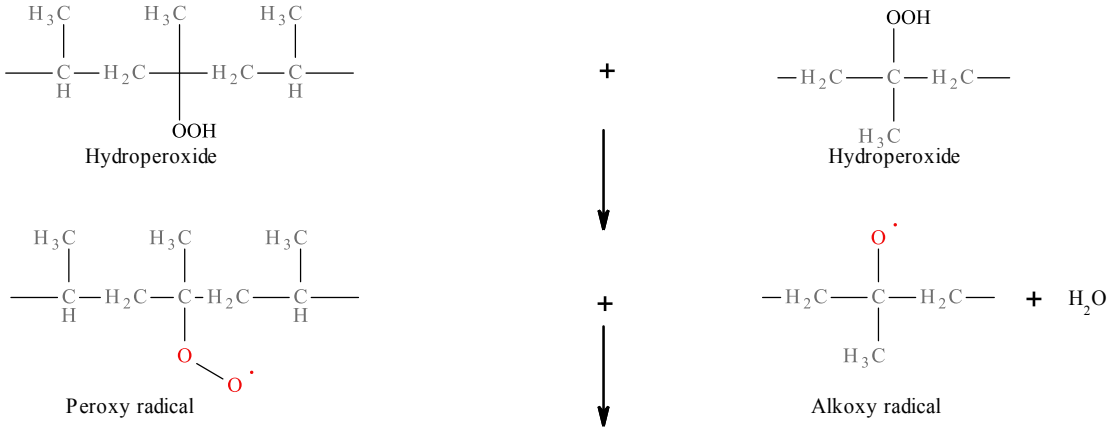
Scheme: 1.5. Unimolecular and bi-molecular decomposition of tertiary hydroperoxides in polyolefin [39].

Due to its simple nature homolytic decomposition of hydroperoxides was treated as the valid explanation in a substantial area of research on polyolefin degradation. Although still known as the predominant mode of hydroperoxide decomposition in photo-oxidative and molten state thermo-oxidative degradation in polyolefin, homolytic decomposition of hydroperoxide is negligible in thermo-oxidative degradation of solid-state polyolefin.

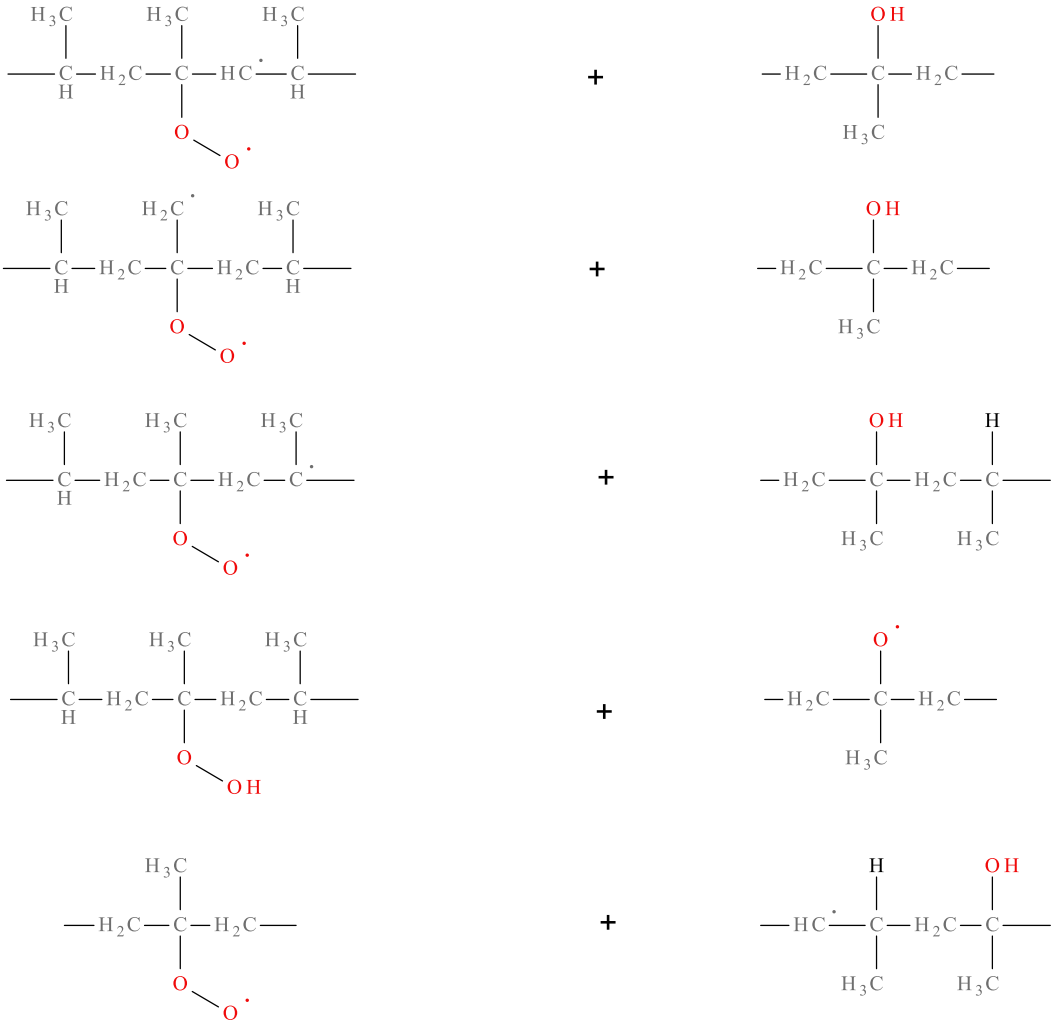
Heterolytic decomposition of hydroperoxides is a bi-molecular reaction of inter and intramolecular nature. For PP, it primarily involves two tertiary hydroperoxides combining into an unstable complex, eventually breaking into alkoxy and peroxy radicals (Section: 1.5). In gaseous and liquid state hydrocarbon systems, the products of heterolytic bimolecular decomposition mainly proceed to follow their individual reaction pathways. For solid-state systems and low temperature conditions degradation in polyolefin, it carries important implications. Semi-crystalline materials like PP, for example, demonstrate a so-called cage-effect, which implies that the mobility of any isolated species in the polymer is limited. In this situation, there is a strong probability for the immediate products of the thermo-oxidative degradation to be engaged in further reaction. Such reaction, again, can be inter and intramolecular in nature and the possibility are numerous (Scheme: 1.6). The cage-effects

propose alternative explanation for the formation of important carbonyl emissions, e.g. aldehydes, and ketones, during PP degradation [40-42].

Bimolecular decomposition of hydroperoxides in a solid-state PP matrix



Cage-reactions among the free radicals resulting from hydroperoxide decomposition in solid-state polymer



Scheme: 1.6. Cage Reactions among the bimolecular decomposition reaction products of hydroperoxide [43].

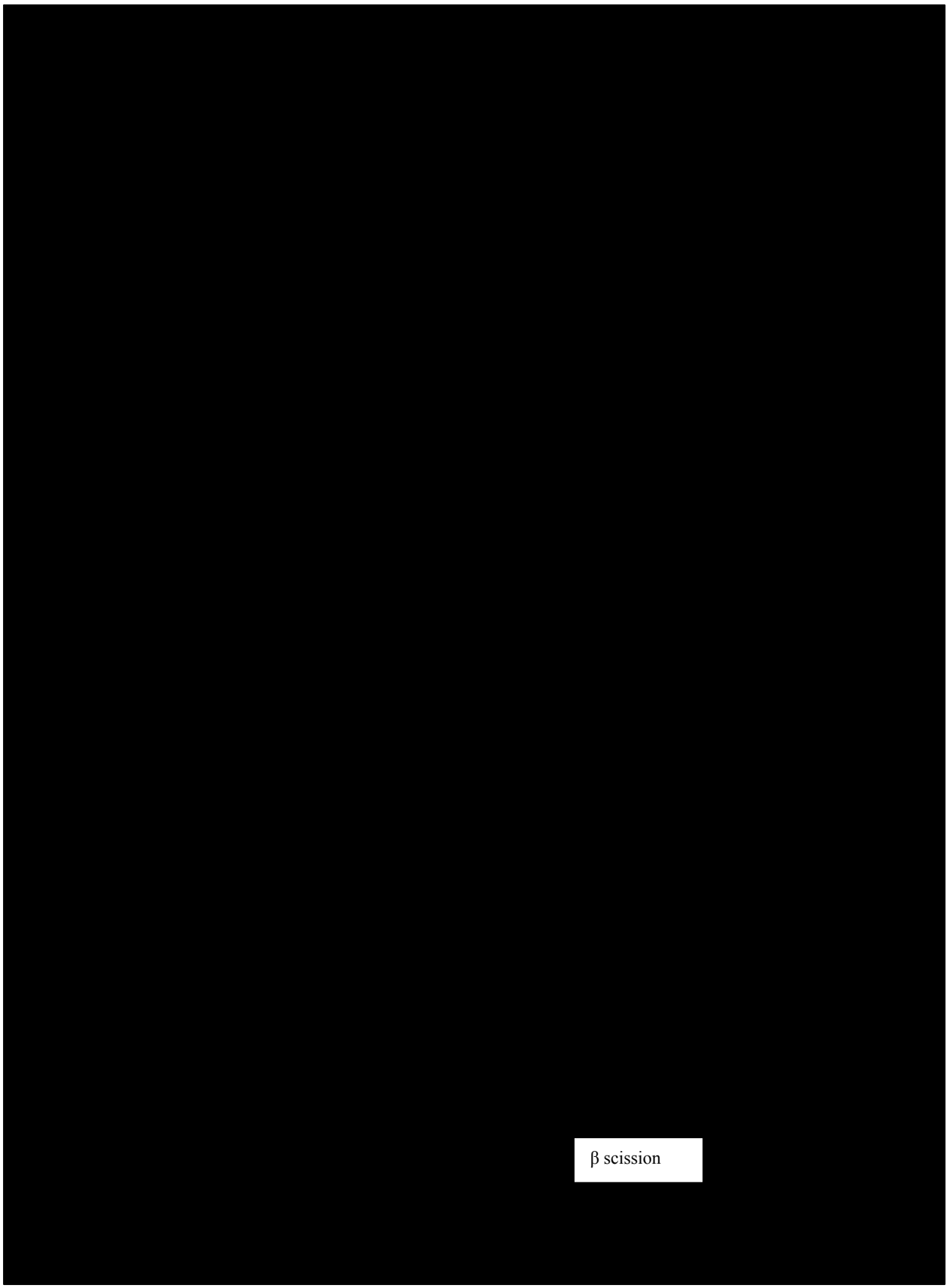
Conventionally, aldehydes have been described to be generated by oxidation of primary and secondary alkyl radicals (Scheme: 1.12 and Scheme: 1.17). In PP however, primary and secondary alkyl radicals form only a minority of the PP based radicals, they are not an ideal basis to explain the omnipresence of substantial aldehyde-based emissions evolving from the polymer PP. Bi-molecular decomposition of hydroperoxides and reactions among the decomposition products provide an alternative explanation of the range of oxidation products characteristic of PP degradation.

1.3.3. Termination

Concentration of free radicals and the non-radical species increases as propagation proceeds. Under sever oxidation conditions, e.g. high temperature etc., the possibilities of the mutual interactions among the radicals also increase many-fold. It is at this stage that radicals get involved in collision leading to their quenching, hence marking the beginning of termination stage of auto-oxidative degradation cycle. Termination occurs through disproportionation and recombination pathways and mainly involves peroxy radicals (Scheme: 1.7). Due to the relatively low concentration left at this late stage of the degradation cycle, only a minority of any alkyl and alkoxy radicals is scavenged during the typical termination reactions i.e. disproportionation and recombination.

Various different reactions that form the termination stage of degradation are summarised as below:

- Instead of undergoing typical recombination and disproportionation reactions, peroxy radicals decompose or isomerise to generate alkyl radicals. The alkyl radicals thus formed quench through recombination and disproportionation among themselves. However, if the concentration of alkyl radicals, is comparable with that of alkoxy radicals, recombination leads to the formation of alky-alkoxy complexes as well. The latter situation is more common in the presence of ample availability of oxygen.
- Peroxy radicals also combine to form a tetroxide complex, which decomposes to give final products. It is the type of the radicals involved in the complex that determines the nature of the decomposition products.
- Peroxy radicals also terminate by abstracting α-hydrogen from the polymeric chain. The radical is eventually reduced into a hydro-peroxide in this case.



Scheme: 1.7. Termination of free radicals in polyolefin through disproportionation and recombination reactions [45].

- Finally, the peroxy radicals can also from alkyl-peroxy radicals, which decompose generating ketones and alkyl radicals.

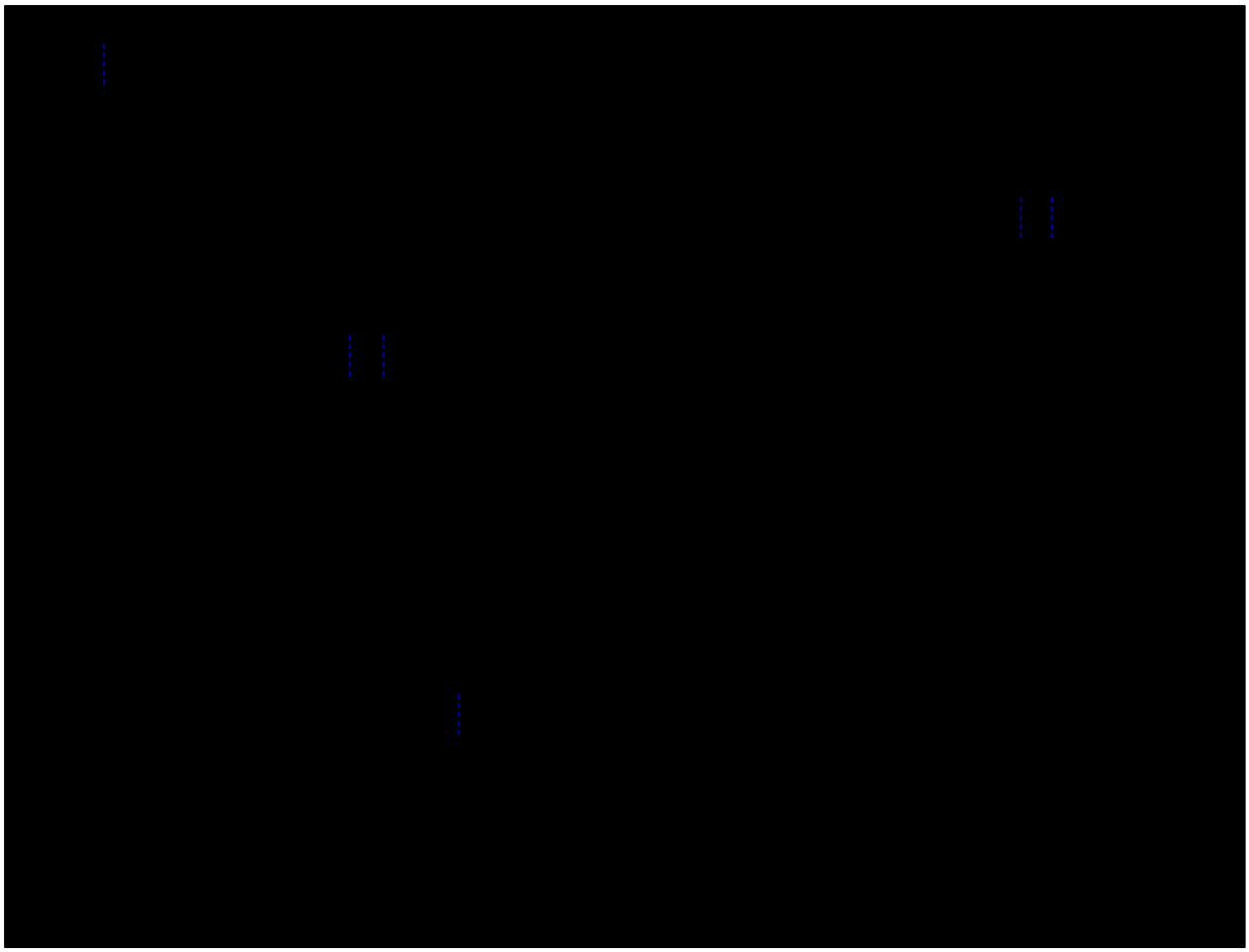
  Termination of alkyl radicals is more important in low pressure of oxygen when their relative concentration is comparatively high. In such situation, they follow typical recombination and disproportionation routes to generate molecular products. At comparatively higher oxygen pressure, they alkyl radicals are oxidised into alkoxy radicals, and the two can combine into alky-alkoxy complexes [38, 44].

1.4. Low molecular weight degradation products of PP

As thermo-oxidative degradation progresses through the polymeric matrix the quantity of various types of free radicals, e.g. alkoxy, peroxy and alkyl radicals, builds up. Increasing concentration of the free radicals leads to an increase in the mutual interactions among them producing another generation of free radicals as well as molecular species. In PP a major part of the molecular products thus generated consists of compounds of low molecular weight, which are volatile and escape the polymeric matrix as emissions [4-6, 30, 31, 46]. The role of the LMWCs/emissions in the chemistry of polymer degradation was realised during very early works on degradation [6, 29]. Their actual analysis, however was not always an easy task and could only be reasonably accomplished with the advent of sensitive and universal analytical tools like GC-MS, and sophisticated experimental methods like solvent-free extraction methods and isotopic labelling techniques [47, 48]. Over the years, various studies have been conducted to trace the origin of various groups of emissions and chemistry behind their formation [39, 49-53]. In conjunction with macromolecular degradation mechanisms, the degradation products have been used for the better understanding of the underlying chemistry of the process [54, 55]. The LMWCs have also been used as a tool for indirect analysis of thermo-oxidative degradation in the situations where direct analysis is not possible, e.g. in paraffin the major part of free radicals are of primary nature and too reactive to be analysed, any molecular products generated by the polymers provide an indirect method to study degradation [29]. Further, the analysis of the LMWCs emitted by polymers allows an assessment of their possible effects on environment [15].

Experiments under various conditions, e.g. ageing temperature, availability of oxygen, effect of processing conditions, and exposure to UV-light etc. have shown that emissions from PP are affected by external as well as internal factors. Increase in temperature, for example, has been shown to have direct effect on the emissions from the polymer, in general [14]. Acetone and acetaldehyde, two important degradation products generated during thermo-oxidative degradation of PP however, have been reported to maintain their relative proportion irrespective of the ageing temperature. It has been reported that decrease in oxygen availability or in its diffusion leads to formation of olefins, diens and aromatic emissions among others [56, 57]. Although aldehydes, acids, alcohols, esters and ketones have been reported among the emissions from PP, the nature of individual compounds has been found to vary, mainly due to the variations in the experimental conditions [44, 52, 54].

Despite the comparatively large number and range of the LMWCs that have been reported as the degradation products of PP, studies that focus on the underlying chemistry for their formation tend to focus on a rather limited number of compounds. As shown in the Scheme: 1.8, acetone, acetic acid, acetaldehyde, diketones, methyl ketones and methyl acrolein, for example, is the group compounds that has mainly been reported in the literature on emissions from PP [58, 59].



Scheme: 1.8. Reaction mechanisms for the formation of the key carbonyl compounds in PP [59].

Further, the chemistry of the emissions from PP has primarily been discussed mainly in the context of un-stabilised form of the polymer, hence mainly accounting for the un-inhibited form of thermo-oxidative degradation [60]. Such approach can be appreciated for its simplicity and convenience in analysis but does not necessarily carry much implication for degradation during service life conditions of the polymer as the polymer is hardly ever used in its un-stabilised form. The studies that take the stabilisation factors into account focus on very basic stabilisation i.e. SN1680 and SN1010, and the discussions tend to touch the topic in a more cursory manner [52, 53]. It is this important void in the literature on PP degradation/emissions that is to be bridged

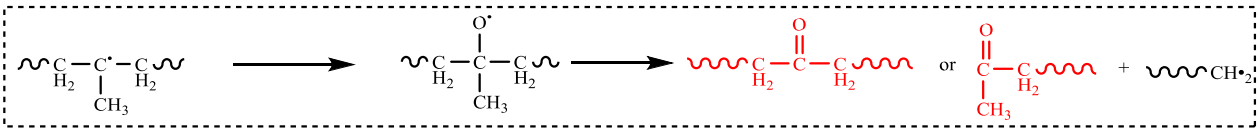
through the current work. A comprehensive review of the relevant scientific literature, especially on the chemistry of PP based emissions is very important to set a framework against which any new data/observations could be discussed. The rest of the current section therefore, is mainly a review of the chemistry behind the key groups of emissions generated by PP during its thermo-oxidative degradation.

1.4.1. Ketones

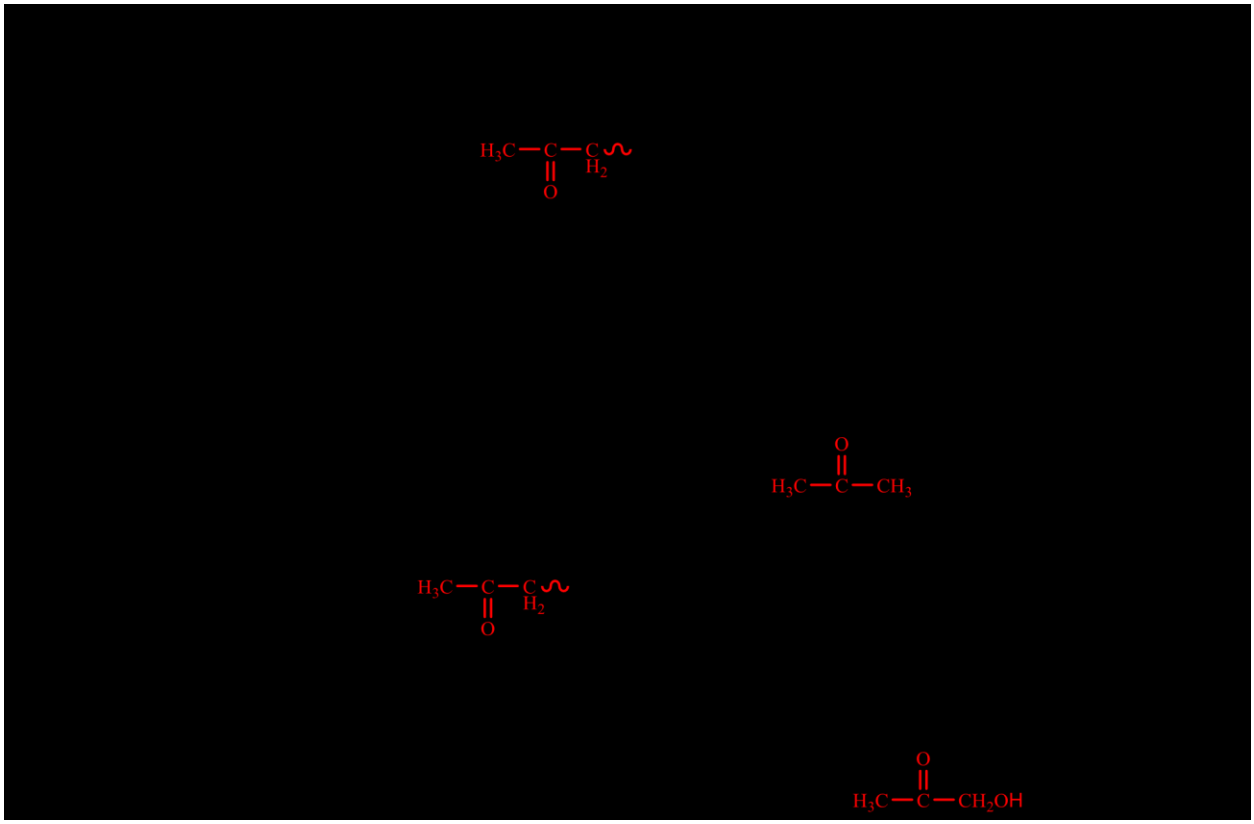
In PP, ketones are mainly formed by tertiary alkoxy radicals. Their formation can be described by two different approaches.

- The first approach considers the formation of ketones from the alkoxy radicals generated by decomposition of isolated hydroperoxides along a polymeric chain (Scheme: 1.9). The alkoxy radical thus formed can cleave along the methyl branch or polymer main chain generating main-chain ketone and methyl ketone respectively. The formation of methyl ketones is facilitated by the presence of unsaturation in proximity of the alkoxy radical in a polymeric chain. Alcohols and acids are formed as important by-products of such reactions (Scheme: 1.10 and 1.11).
- The second approach focuses on the hydroperoxides formed as sequences, and is of special relevance to PP due to high proportion of the hydroperoxide sequences in the polymer. In dihydroperoxides, the hydroperoxides at alternating carbons along a polymeric chain have been reported to lead to diketones, while those on the consecutive carbons generate methyl ketones (Scheme: 1.11).

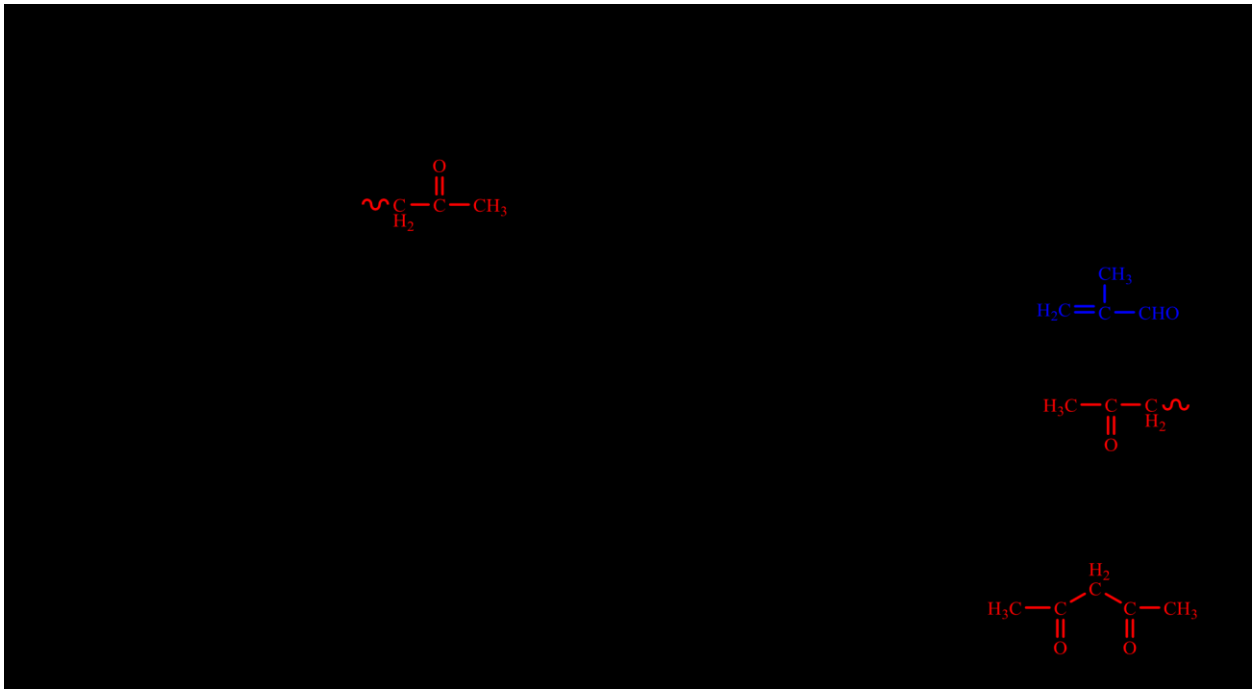
In PP degradation, the relatively high importance of ketones is also linked to their role as precursors for various further reactions. Methyl ketone, for example, is reported to act as a precursor of acetone, methanol, methane, and carbon mono and dioxide [58, 61]. In addition to the tertiary alkoxy radicals, secondary alkoxy radicals are also involved in the formation of ketones, while the primary alkoxy radicals are mainly known for their role in the formation of aldehydes and α-methylated carboxylic acids (Scheme: 1.13) [9, 59, 61].



Scheme: 1.9. Formation of methyl and end-chain ketones.



Scheme: 1.10. Formation of ketones and alcohols from alkoxy radicals.

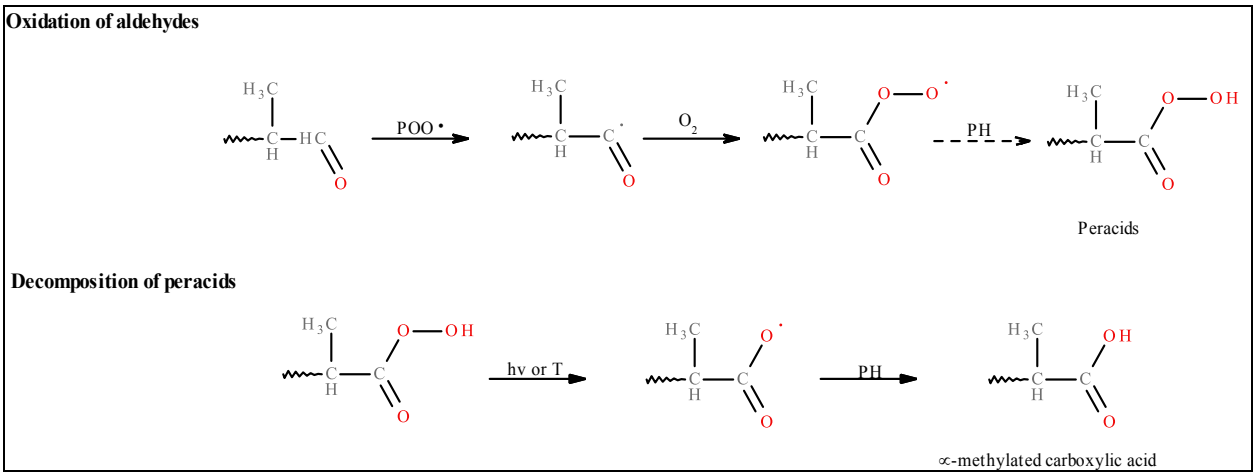


Scheme: 1.11. Formation of methyl and end-chain ketones from the alkoxy radicals (other than the Scheme 1.9).

Scheme: 1.12. Chain scission of primary and secondary alkoxy radicals forming corresponding ketones and aldehydes.

1.4.2. Aldehydes

Unlike ketones, aldehydes are formed by β-scission of primary and secondary alkoxy radicals [38, 59].



Scheme: 1.13.Formation of α-methylated carboxylic acids from primary alkyl radicals in PP degradation [39].

In secondary alkoxy radicals, aldehyde formation is subject to competition between β-scission and hydrogen abstraction pathways leading to the formation of aldehydes and ketones respectively (Scheme: 1.12). Although no such competitive reaction pathway is reported for the primary alkoxy radicals, their role in the formation of aldehydes is limited by their isomerisation into corresponding relatively more stable secondary forms. The yield of aldehydes at a given stage during degradation is also limited by their further oxidation into α-methylated carboxylic acids. (Scheme: 1.13.). Despite their established presence among the emissions from PP, the role of aldehydes in PP degradation has not been discussed as it ought to be. It can be due to the fact

that the aldehyde formation is predominantly associated with oxidation of primary and secondary free radicals, the radicals generally considered too low in extent to considered for sufficient degradation role during PP degradation [29].

1.4.3. Alcohols and Esters

Alcohols and esters are reported as two important groups of emissions generated by PP. Alcohols are formed by multiple pathways, mainly large molecules that stay inside the polymeric matrix. The alcohols react with acid through condensation reactions forming esters.

Last but not least are the carbon monoxide and carbon dioxide. The two gases are usual products of degradation processes in materials of natural and synthetic nature. Formation of carbon monoxide and dioxide begins with primary and secondary alkoxy radicals generating aldehydes. The aldehydes on further oxidation form carbon monoxide and carbon dioxide. Proposed recently, this explanation is comparatively simple and will be reassessed for the presence of the range of the stabilisation packages used in PP formulations for the current work [59].

1.4.4. Carboxylic acids

Carboxylic acids can be formed by oxidation of primary aldehydes, and oxidation of secondary and tertiary alkoxy radicals as well as secondary products formed by interaction among the primary products of oxidative degradation, e.g. alcohols and aldehydes etc.

1.4.5. Hydrocarbons

Hydrocarbons are the major products of thermal scission in PP. For the degradation studies however, they have not been the primary focus, and have mainly been the subject of polymer pyrolytic investigations. Due to obvious differences in the experimental conditions of a pyrolytic and a solid-state ageing of the polymer the results cannot be compared in a straightforward way. In general the hydrocarbon-based emissions from PP have been reported to consist of methylated alkanes, alkenes and dialkenes. They are mainly generated as a result of random chain cleavage, intramolecular hydrogen transfer, and β-scission reactions [27]. In the current study, the aim is to conduct an all-inclusive analysis of the emissions from PP and reveal any patterns in the hydrocarbon emissions from PP degradation as well as the oxidation products of the polymer.

1.5. Stabilisation of Polypropylene

The propensity of PP to degradation makes it imperative that the polymer is adequately stabilised with an appropriate combination and concentration of antioxidants/stabilisers [3]. Our understanding of stabilisation of polyolefin has grown almost in parallel with that of degradation of the polymer. Initially when oxidation was defined mainly as formation of the mal-oxides, stabilisation was described as simple scavenging of the mal-oxides. Later, the proposal of 'free radicals chain theory' redefined the role of antioxidants as free radical scavengers. Now it is a common knowledge among the polymer research community that the stabilisation mechanisms are individual to the stabiliser groups, and far from a generalised mechanistic pathway [38]. Stabilisation capacity of a given antioxidant mainly depends on its physiochemical properties, stabilisation mechanism, and nature of the stabilisation reactions as well as any side reactions. The side reaction, for example, thermal degradation, oxidation and various types of transformation reactions, can convert the parent antioxidant into species with antioxidants or pro-oxidant character. The nature and relative concentration of such species plays an important role in determining the overall stabilisation capacity of an antioxidant during polymer service life. Due to the multiple free radicals that require scavenging, an antioxidant is hardly ever used on its own. Commonly, multiple antioxidants form a stabilisation package to provide protection at various stages and against various types of free radicals. The selection of the individual antioxidants in a stabilisation package is determined by their mutual compatibility as well as end-product applications of the polymeric formulations. The interactions among various groups and individual antioxidants can be positive resulting in higher cumulative stabilisation, or negative causing a depletion in the stabilisation capacity expected of the individual antioxidants. The former is known as synergism and the latter as antagonism [10, 19, 38].

Stabilisation in its simplest form is described as scavenging of free radicals by appropriate set of compounds i.e. antioxidants, which are incorporated into a PP matrix prior to processing. Different groups of antioxidants work through different mechanisms to achieve the same goal of stabilisation. The choice of stabilisers for a given PP based application is determined by multiple factors including the stabilisation characteristics of the antioxidants as well as the service life conditions of the end-use applications. Besides, antioxidants have their specific temperature limits, within which they can operate, thioesters, for example, generate stabilisation at low temperature i.e. > 150°C and are not therefore appropriate for stabilisation during processing and in applications with high temperature service life conditions. Phosphite and hydroxylamine

antioxidants, on the other hand are active at high temperature and inactive at low temperature. Protection against thermo-oxidative degradation is required during service life as well as against the stresses of processing conditions i.e. high temperature, mechanical shear etc. the stabilisers are therefore incorporated prior to processing. PP stabilisation, like the degradation of the polymer, is a complex process and one way to look at it is from the perspective of the stabilisation mechanisms of important groups of antioxidants [10, 19, 38, 62-64]. The range and total number of stabilisers developed for PP is too wide to be covered in the current study, for now only the groups that are used in the experimental work for the current study are discussed.

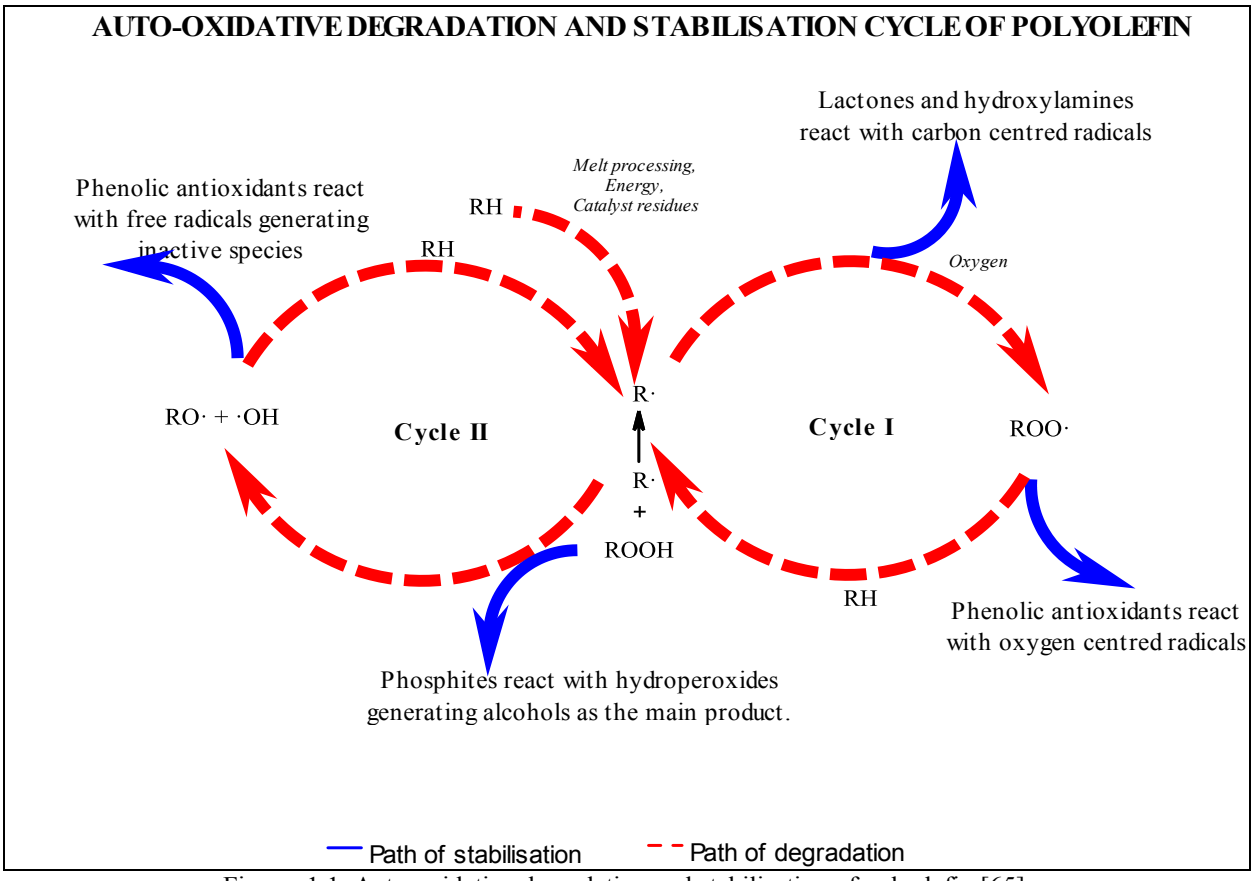


Figure: 1.1. Auto-oxidative degradation and stabilisation of polyolefin [65].

1.5.1. Antioxidants

Since the first synthetic antioxidant that was used to stabilise rubber more than half a century ago, extensive research in the area of polymer stabilisation has led to the development of a range of antioxidant groups with versatile physiochemical properties. Primarily, as scavengers of free radicals in a PP matrix, the antioxidants are conventionally classified into primary and secondary antioxidants. Each group of the antioxidants works by a specific chemical pathway scavenging a

particular group of free radicals generated during different stages of the auto-oxidative degradation cycle (Figure: 1.1).

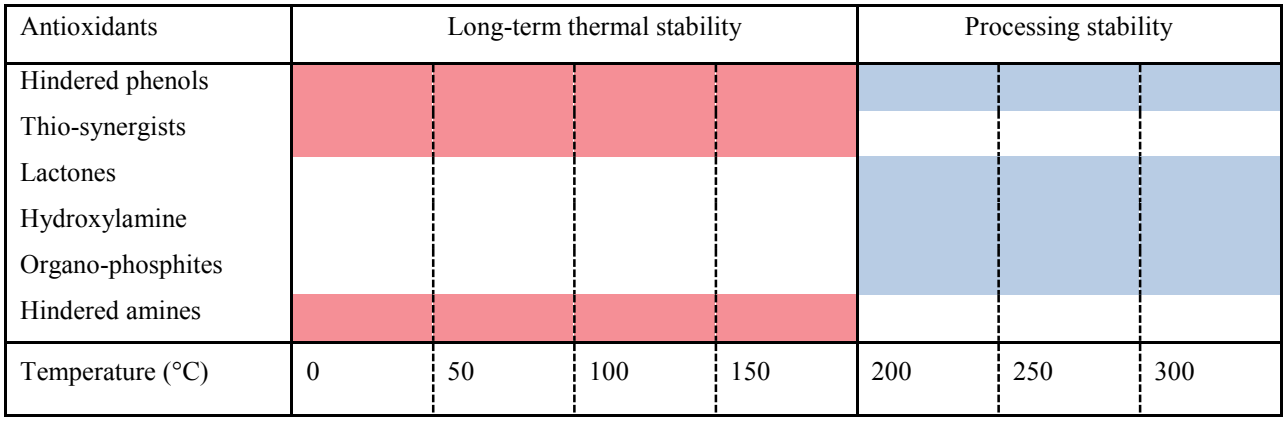


Figure: 1.2. Key antioxidant groups for polyolefin stabilisation and corresponding active-temperature zones [45].

Phosphites, lactones and hydroxylamine are high temperature stabilisers used to provide protection to the polymer during processing, while thioesters and hindered amines are mainly used for stabilisation during service life in the appliances for low temperature applications (Figure: 1.2). Hindered amines are apparently the group with the widest zone of operation i.e. capable of providing stabilisation under service life and processing conditions [3, 63].

1.5.1.1. Primary antioxidants

Primary antioxidants scavenge free radicals generated during propagation stage of auto-oxidative degradation cycle. Alkyl, alkoxy and peroxy radicals are converted in hydroperoxides as a result of reduction by the primary antioxidants. The relative reactivity of the hydroperoxides is significantly less than the –oxy free radicals (alkoxy and peroxy radicals), their decomposition therefore requires another episode of stabilisation by secondary antioxidants. Hindered phenols, hindered amines and thiobis-phenols are the commonly used groups of primary antioxidants that can further be divided into chain-breaking electron acceptors and chain-breaking electron donors. The former group mainly scavenges alkyl radicals by accepting the unpaired electron from the free radical, while the latter scavenges alkoxy and peroxy radicals by donating hydrogen atoms to free radicals. A hydrogen donor is capable of donating hydrogens with greater ease than it could be extracted from a polymeric chain, hence inhibiting the formation of any more alkyl radicals [27, 45, 65].

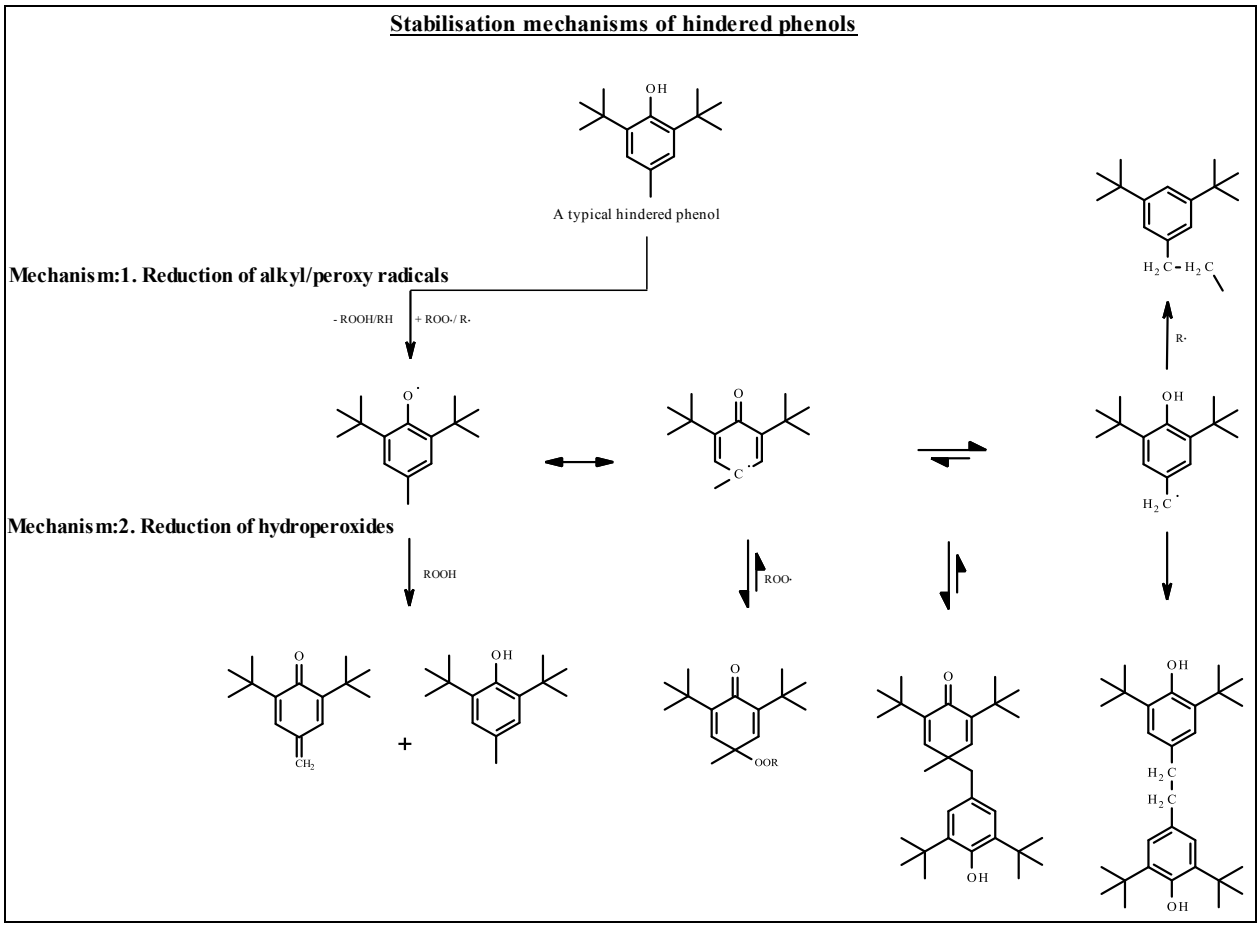
1.5.1.1.1. Hindered phenols

Hindered phenols are a group of primary antioxidants commonly used as melt and service-life stabilisers in polyolefin. It comprises of a range of compounds with diverse chemical structures. The scavenging of free radicals by hindered phenols is a fast reaction with the reaction rate in the range of 10^{-7}-10^{-9} s. As shown in the Scheme: 1.14, a phenolic during its stabilisation mechanism is converted into phenoxy radicals, which undergo self-stabilisation through internal delocalisation of electrons. Any peroxy radicals inside a polymeric matrix are converted into hydroperoxides by the hindered phenol. The conversion of peroxy radicals into hydroperoxides, comparatively less reactive chemical species, inhibits the rate of degradation. The 'phenol-phenoxy' stabilisation mechanisms of hindered phenols has been experimentally confirmed by methods like isotopic labelling of the hydrogen, identification of the phenoxy radical by EPR, and last but not least, by decrease in chemiluminescnece emissions intensity as a consequence of chain termination by the hindered phenol. Further, an inverse relation has been found to exist between the concentration of hindered phenol and rate of thermo-oxidative degradation.

The chemical structure of a hindered phenol has a key role in the stabilisation it can generate. Fully hindered phenols, for example, are better at stabilisation than partially hindered, while the unhindered phenols are the least efficient. The chemical nature of substituents on the aromatic ring of a hindered phenol also affects the hydrogen donation ability of the antioxidant. It is mainly associated with their effect on the bond dissociation energy of the O-H group, and interaction (coupling and hydrogen bonding) of the antioxidant with other components of a polymeric formulation. Due to higher chances of hydrogen bonding between the O-H bond and the hydrogens on the -ortho and -para position of the aromatic ring in a hindered phenol, unhindered phenols are hardly ever used as stabilisers. Among the hindered phenols, the stabilisation capacity or hydrogen donation of a given hindered phenol decreases with increase in the steric hindrance steric hindrance provided by the substituents. Smaller substituents, on the other hand, also promote coupling between phenolic groups. A hindered phenol with higher stabilisation therefore involves an optimisation of various structural features of the compound [66].

Among the key problems facing the use of hindered phenols as antioxidants is their degradation and eventual volatilisation, which seriously affects the performance of the antioxidant and

aesthetic properties of the polymer. Some of the degradation products of hindered phenols have also been reported to cause discoloration of the material [27, 45].



Scheme: 1.14. Stabilisation mechanism of hindered phenols [27].

1.5.1.1.2. Hydroxylamines

Hydroxylamines are process stabilisers. They protect polymer degradation by scavenging alkyl radicals and hydroperoxides, thereby acting as primary as well as secondary antioxidant to varying extent. The temperature range within which they operate however makes hydroxylamine more suitable as processing stabiliser and in the applications with high temperature service life (Figure: 1.2). One main difference between the hindered phenols and hydroxylamines is that the latter performs stabilisation over a comparatively longer period and builds it slowly. Hydroxylamine stabilisation works through cyclic process during which the antioxidant is continuously regenerated, while the peroxy radicals are reduced into hydroperoxides (Scheme: 1.15).

1.5.1.2. Secondary antioxidants

Secondary antioxidants are primarily designed for stabilisation during polymer processing but also provide stabilisation during service life conditions. Commonly known as hydroperoxide decomposers, the secondary antioxidants reduce hydroperoxides into relatively less reactive molecular species like alcohols. Antioxidant character of the secondary antioxidants is strengthened by the presence of sulphur or phosphorous as an essential structural element. Some important examples of secondary antioxidants are phosphite, phosphonates and thioethers.

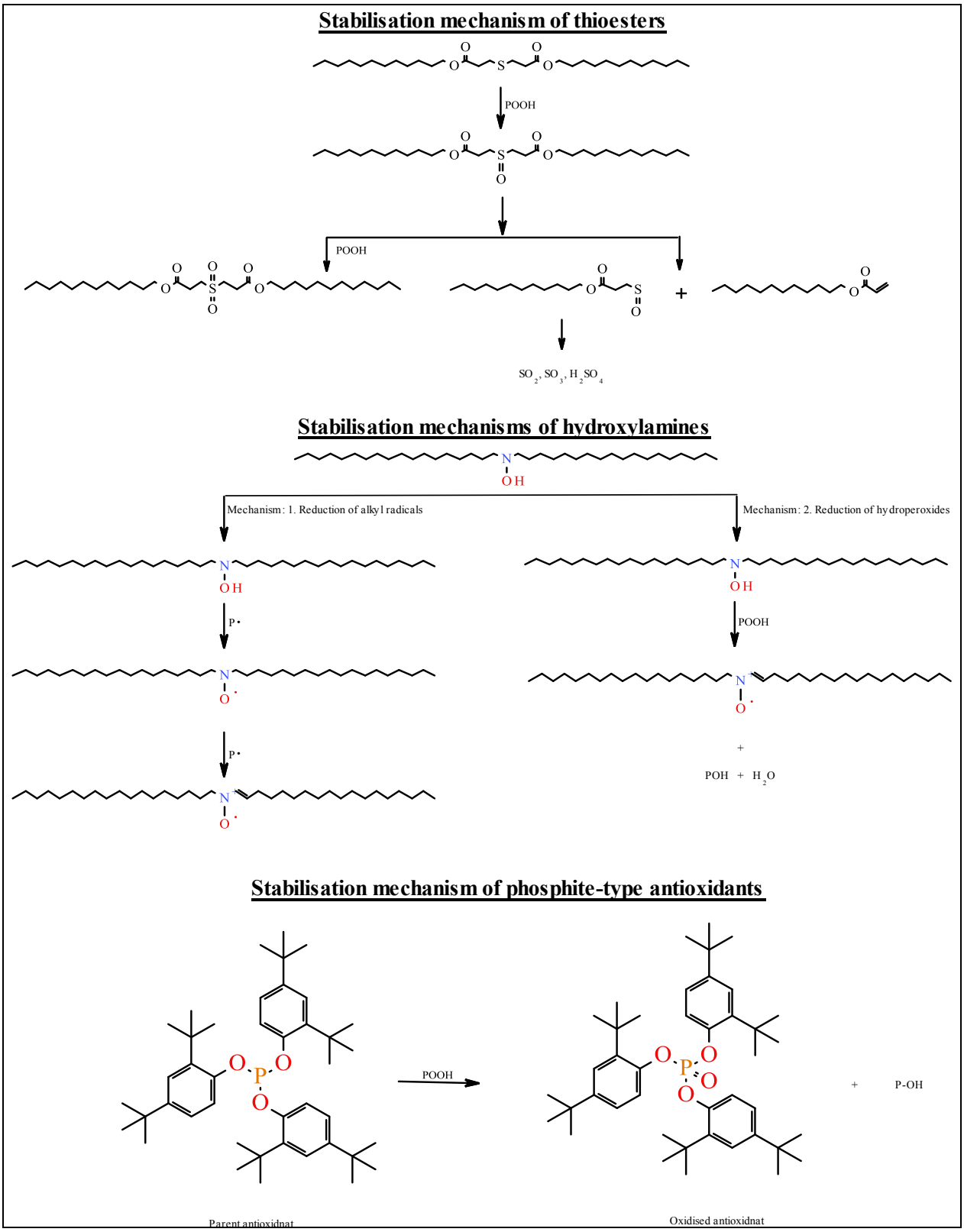
1.5.1.2.1. Organo-phosphites

Organo-phosphites, especially aryl phosphites, are a widely used group of antioxidants. They reduce hydroperoxides while themselves being oxidised into phosphates (Scheme: 1.15). Stabilisation efficiency of the organo-phosphites is '1' making them work only in a stoichiometric manner. In combination with hindered phenols, phoshites form an essential part of stabilisation packages used in commercial applications of polyolefin.

1.5.1.2.2. Thioesters

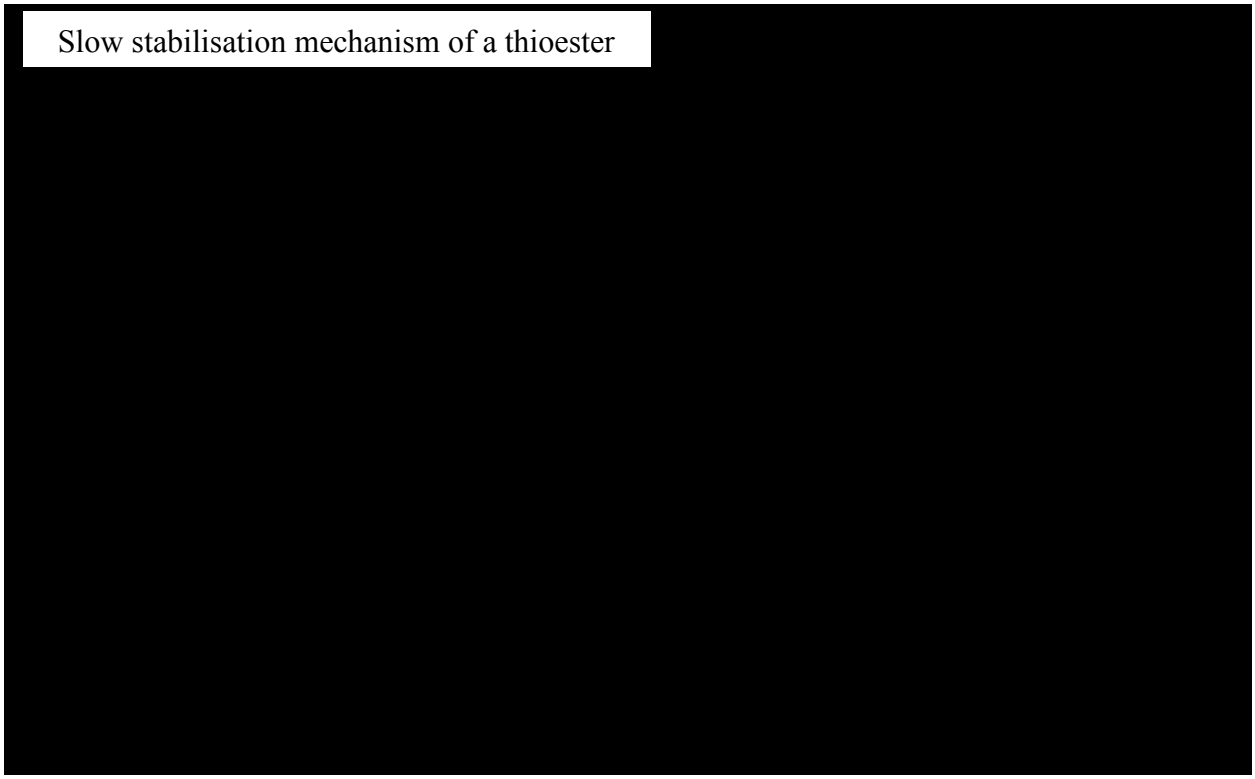
Thioesters are aliphatic esters of β-thiodipropionic acid. Readily oxidisable by hydroperoxides, they form an important group of secondary antioxidants both for processing and service life conditions of polyolefin. DSTDP, DLTDP and SN4120 are some commonly used thioesters used for polyolefin stabilisation.

As shown in the Scheme: 1.16, thioester stabilisation mechanisms are based on non-radical reduction of hydroperoxides into alcohols, while the sulfite group of the antioxidant is oxidised into a sulfonate group. The latter undergoes hydrolysis or hydroperoxydolysis generating a range of transformation products of acidic nature. The acidic transformation products decompose hydroperoxides by an ionic method of catalytic nature, eventually making the thioester-based stabilisation a more efficient, effective, and an over-stoichiometric reaction. The acidic transformation products that have been identified so far include sulfurous acid, sulfuric acid, and various oxides of sulfur [67, 69]. Generated in a very low level, they are very hard to analyse.



Scheme: 1.15. Stabilisation mechanisms of thioesters [67], phenolic, hydroxylamine and organo-phosphites [68].

Among the very few studies that did report their existence, include the work of Billingham *et al*. They detected various oxides of sulphur among the emissions generated by polyolefin stabilised with thioesters, while another research reported sulfones and sulfoxides in PP sample tubes generated by the didodecyl 3, 3-thiodipropionate used as stabiliser in the tubes. The antioxidant capacity of the sulphur oxides has been confirmed by their interaction with cumene hydroperoxides [70].



Fast stabilisation mechanism of a thioesters, catalysed by acidic transformation products of the antioxidant

$$ROOH \xrightarrow{H^+ (SO_2,\ SO_3,\ H_2SO_4)} \text{non-radical products}$$

$$ROH \xrightarrow{H^+ (SO_2,\ SO_3,\ H_2SO_4)} \text{water} + \text{dehydrated products}$$

Scheme: 1.16. Stabilisation mechanisms of thioesters [67].

1.5.1.3. Acids scavengers/additives

In addition to the antioxidants and processing stabilisers, acid scavengers form another important group of additives commonly used in polyolefin. Use of an acid scavenger neutralises any acidic products and catalyst residue, which might hinder the performance of hindered phenols. The selection of an acid scavenger is based on its purity, thermal stability, price-performance ratio, compatibility with the polymer matrix, its melting point and particle size etc. Some common examples of acid scavengers used for polyolefin matrices are calcium stearate, calcium lactate and zinc oxide. Calcium stearate, although an effective acid scavenger for Ziegler-Natta based polyolefin, is hygroscopic and cannot be used in some applications. Calcium lactates form chelates with trace metal impurities but due to thermal instability, cannot stand the high temperature.

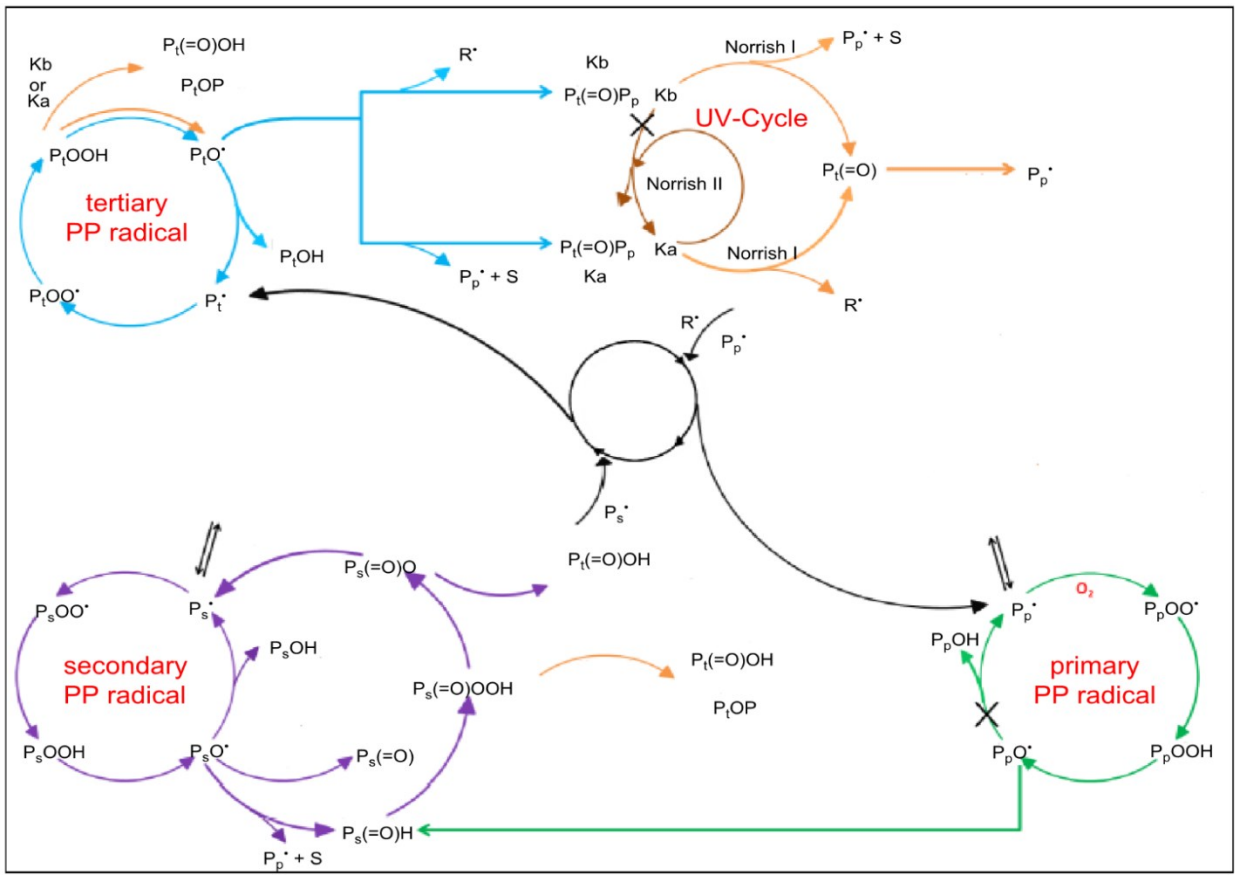
The performance of a metallic stearate, e.g. calcium stearate is affected by factors like processing technology, heat history and the degree of reaction, and can be a cause of mild fatty odour in stearates. The fatty nature of CaSt makes it work both as an acid scavenger and as a lubricant. The lubricity however, needs to be critically judged in applications where surfaces and moulded parts are subsequently coated with lacquers, e.g. in automotive applications. In addition to their applications as acid scavengers and mould release agents, CaSt also works as dispersion aid for fillers, pigments and reinforcements. The second important acid scavenger is zinc oxide, which is used in polyolefin both as an acid neutraliser and as a UV-light stabiliser. The acid scavenging capacity of ZnO is more than the same weight of CaSt (due to the low molecular weight of ZnO). ZnO, however, does not have the property of colour hold and can impart opacity up to 10%. The lack of lubricity by ZnO also requires an additional lubricant in higher temperature applications. Other than the additives a range of fillers and pigments are used to form tailored made end-use PP application [19].

1.6. Kinetics modelling of thermo-oxidative degradation in PP

Chemical kinetics are vital to understanding of a chemical reaction or a chemical process. For polyolefins, a useful approach lies in capitalising kinetic parameters, e.g. rate constants, reaction energy and reaction rate etc. in the form of non-empirical kinetic models. Based on the fundamental mechanisms of thermo-oxidative degradation, such models are meant to be a numerical tool for polymer lifetime prediction and are means of investigating the process with regard to multiple intrinsic and extrinsic factors that can affect the process [12, 39]. Since the pioneering work of Tobosky, a significant development has been made on kinetic modelling for polyolefins. Based on a simple set of assumptions and the key stages of thermo-oxidative degradation, Tobosky derived and solved corresponding rate laws using conventional kinetic methods. The model proved very useful in predicting thermal, photo and oxidative degradation in polyolefin and paved the way for further works. In later works, the kinetics models of polyolefin degradation were extended to include most of the reactions of polyolefin degradation process. As a next step, the model was modified for specific types of degradation through an alteration of the basic assumption [30]. At this stage the models were capable of explaining the role of oxygen in determining the rate of polymer degradation, and profiling the eventually formed oxidation products. Any further works were aimed at enhancing the robustness of the existing analytical models mainly by simplifying the assumptions underlying the models.

A major development in kinetic modelling was the emergence of new algorithms in the 1980s, which made it possible to solve complex equations and hence, opened new avenues in kinetic modelling by allowing solution of the equation not previously possible with the conventional methods. Taking full advantage of the new algorithms, almost all possible chemical reactions were carefully worked out and incorporated into a comprehensive model [71]. The validity of such models, however was called into question due to unavailability of the required reliable kinetic parameters; it was impractical to determine all kinetic parameters for all elementary steps. The next step was to cut the mechanistic schemes short to the level of reactions of critical importance only, giving rise to the idea of ‘critical reaction pathways’. This approach is based on replacing multiple elementary reaction with a hypothetically equivalent reaction. Applying this strategy to the auto-oxidative cycle of degradation gave rise to a scheme known as closed-loop mechanistic scheme of universal scope (Scheme: 1.17). This scheme is based on hydroperoxide decomposition as the origin of all radicals, and treats primary, secondary and tertiary carbons as different reactions sites along a polymeric chain [72, 73].

PP has been widely investigated for kinetic modelling. While these models target various areas of degradation they tend to focus more on un-stabilised form of the polymer [74]. The scope of such studies therefore is limited in the context of their implications for service life conditions of the polymer; as the polymer is hardly ever used in its un-stabilised from in its real life conditions. Further, there is need for better understanding of stabilisation mechanism of antioxidants. The existing concepts about stabilisation are unable to explain high stabilisation achieved with small quantities i.e. 1%, of the antioxidants. Further, a correlation of the stabilisation mechanisms with their kinetics, while present inside a PP formulation, is an area that need to be investigated in more detail.



Scheme: 1.17. Closed-Loop mechanistic scheme for the prevalent reaction pathways in the thermo-oxidative degradation of PP [39].

1.7. Experimental Methodology

Changes in the physical properties and chemical structure of PP are two common criteria used to study degradation in the polymer. Changes in the physical properties, e.g. mechanical strength etc. have long been used to test polymer durability and for life-time prediction, and still form the basis of a range of tests commonly used in polymer industry. For research purposes, the physical property testing is not an ideal criterion. In most of the cases change in a physical property does not appear until very later stage of polymer degradation, and hence require accelerated ageing. The accelerated ageing not only results in omission of the information on the early degradation stages, but is also under debate for its applications in real-life degradation conditions of a polymer. Further, any data derived from physical testing does not carry much information about degradation chemistry, e.g. nature of the degradation products and associated reaction pathways etc. [7]. Over the years, with the development of better analytical techniques, chemical analysis has becomes more acceptable experimental approach to study polymer degradation, and a range of spectroscopic techniques have been adopted as conventional methods in the polymer laboratories. IR, CL and UV spectroscopic methods, for example, are now routinely used to study degradation in polymeric matrix, while chromatographic methods have become the common choice for emissions analysis [3, 7, 54, 75]. In the current work, IR and CL spectroscopic methods have been used to investigate thermo-oxidative degradation in solid-state and molten form of PP, while the emissions have been analysed by GC-MS based methods [3, 12, 54, 71, 76].

A cursory review of the major spectroscopic techniques, e.g. UV-visible spectroscopy, IR and CL spectroscopy, shows that any given technique has its own advantages and disadvantages. UV-visible spectroscopy, for example, although simple in operation and an easily available piece of equipment in analytical laboratories, is limited to the analysis of UV-active species. In PP degradation, relatively low UV-absorption by the degradation products and significant interference by the polymeric absorption in the UV-region cause complications. In various studies, the problem has been simplified by converting the spectra into their higher order derivatives. The same strategy has been adopted for the current study but only with limited improvement [3, 77, 78]. The experimental work has mainly been conducted using IR, CL and GC-MS based methods. The sections that follow discuss all three techniques in detail.

1.7.1. Fourier transform infrared spectroscopy

FTIR spectroscopy is an important technique that has long been used for polymer analysis. In a typical IR scan an incident beam is allowed to transverse a polymeric sample. The reflected beam processed by a fourier-mathematical-operation contains absorptions corresponding to the molecular and rotational vibrations of the polymer. The qualitative and quantitative features of an IR spectrum change with the change in the chemical composition of the polymer during its degradation [79]. The use of IR spectroscopy for polymer analysis has improved with the advent of a more convenient ATR-based sampling method.

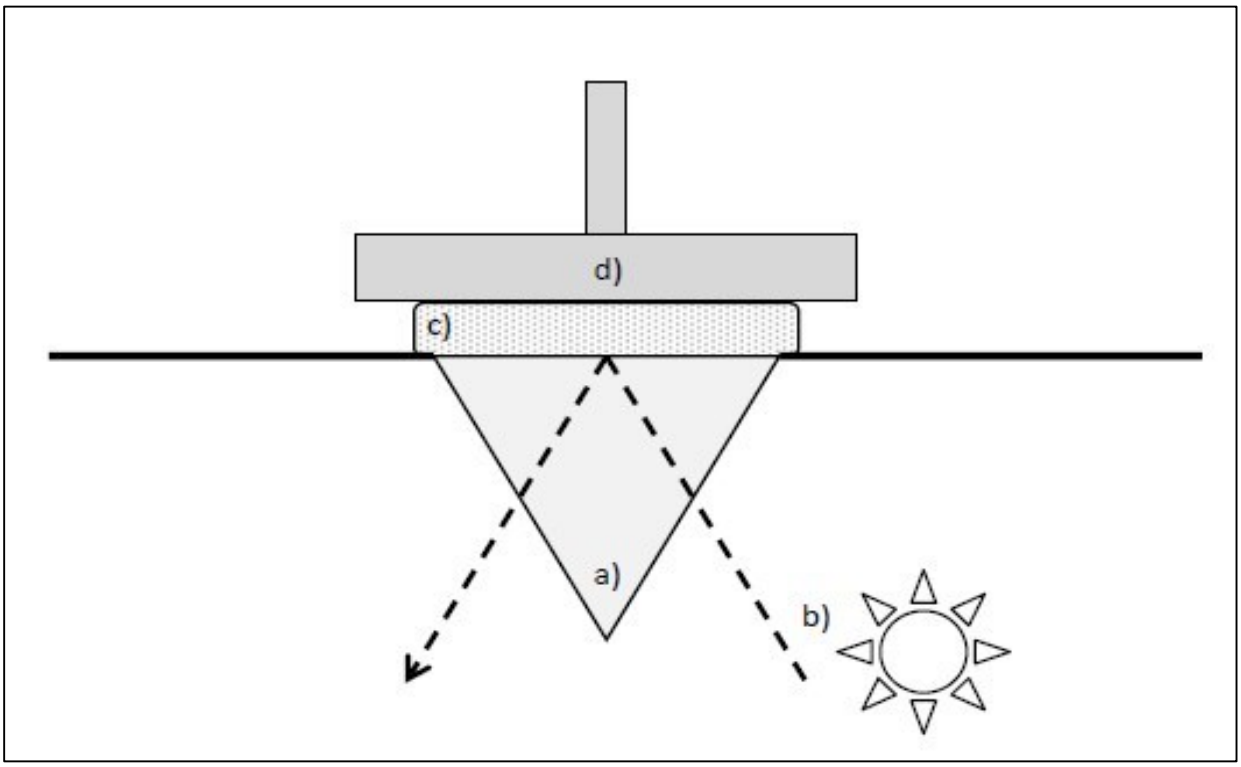


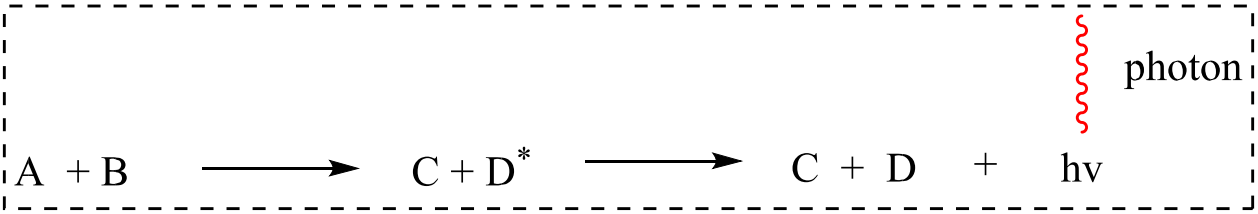
Figure: 1.3. An ATR cell used in ATR-IR spectrophotometers. (*a; diamond prism, b; light source, c; sample, and d; applied pressure to make a thin film*) [45]

A typical ATR-IR instrument is improvised with an ATR cell operating on the principle of attenuated-total-reflectance. The ATR cell is made of a material of reflective index higher, e.g. diamond, than that of the material to be analysed, allowing total-reflectance of the incident beam (Figure: 1.3). In a typical ATR-IR experiment, the sample is placed on the ATR window i.e. the surface of the diamond exposed to environment and pressed into a thin layer under the pressure of an overhead pressing arm. Incident IR wave passes though the diamond scans the sample surface that is in contact with the diamond, and is totally reflected back into the diamond to be detected by photomultiplier tubes [80]. An IR peak typical of PP that appears at 2720 cm^{-1} is

generally associated with bending and stretching vibration of the C-H and -CH_3 bonds. Relatively pure and stable, this peak is often used as internal reference when quantitative analysis of degradation in the polymer is done (Figure: 3.4) [7, 78, 80-82].

1.7.2. Chemiluminescence spectroscopy

In 1961, Ashby discovered emission of weak visible light from degrading polymers. The emission detectable by photomultiplier tubes, was found to bear a correlation with the oxygen absorbed by the samples, and was characteristic of the type and chemical nature of the polymer [83]. Later denoted by chemiluminescence (CL) [84], it formed the basis of CL spectroscopy. Currently CL emission is described as the surplus energy emitted during the deactivation of initially thermally activated products of a chemical reaction (Scheme: 1.18). CL emission has been demonstrated to bear a quantitative relation with any underlying CL-active reactions [85-89].



Scheme: 1.18. Generalised mechanism of CL emission. 'D*' is the product that is initially formed in an activated state deactivating to 'D' after emitting surplus energy as a CL signal [90].

As CL spectroscopy developed further and became an analytical tool for polymer analysis it was demonstrated that thermal and temporal variation in the qualitative and quantitative aspects of the CL emission spectra can be associated with various chemical species that are formed as intermediates of thermo-oxidative degradation process. Various research groups investigated such trends in an attempt to use them to develop an explanation of thermo-oxidative degradation and the phenomenon of CL emission itself. After accounting for the experimental conditions and variations among the samples used, the results of such studies were coherent in general. For PP, for example, emission bands at the same wavelength, e.g. 420 nm and ≤ 500 nm, were repeatedly reported. Over time, the spectra were observed to undergo a red-shift i.e. an increase in the intensity of the bands in the higher wavelength region i.e. 420-520 nm, with a simultaneous decrease in intensity of the region 340-420 nm [84, 90-92].

The commonly observed temporal red-shift in the CL spectra has been mainly explained by two different approaches. In the first approach, temporal evolution of new intensities is proposed to be resulting from the new species of secondary nature that are formed overtime. The second approach on the other hand is based on the infection-spreading model of oxidative degradation in polyolefin. It assumes that initial predominance of the low wavelength region is associated with the isolated carbonyls formed in the initially infected spots. The initially isolated carbonyl based emissions prevail until the whole area is fully oxidised, beyond that point conjugated and long chain carbonyls start developing. It is the long chain and the conjugated carbonyls that appear as the longer wavelength region in the CL spectrum. A slight adaptation of the spread model explanation explain the higher wavelengths emission as absorption in re-emission of the initial CL emission. While the former approach discard any emissions > 500 nm as noise originating from geometrical variation in the sample, the latter regards it as the emission generated by the additional build of the oxidation species in the region initially oxidised by small and isolated carbonyl groups. The explanation is interesting but still inconclusive [43, 84, 92-95].

Another area of CL-based research focuses the polymer in its stabilised form. The studies that target CL behaviour of the stabilised form of PP regards the technique a sensitive and accurate method to measure stabilisation capacity of different antioxidants. Decay in CL emission as a polymer is stabilised has demonstrated a correlation with the decrease in the concentration of hydroperoxides [96-99]. The effect of physiochemical features of antioxidants on the stabilisation of polyolefin has also been investigated using CL spectroscopy, but the studies are very few and based only on a few hindered phenol-based packages. In some studies, the technique is described to have some limitation due to possible CL emission from the antioxidants and difficulty in differentiating the emission from each part of a formulation [88, 92, 95].

Although still a relatively new technique, CL spectroscopy addresses many of the problems facing conventional spectroscopic techniques used for thermo-oxidative degradation studies of synthetic polymers, e.g. UV-Vis and IR spectroscopies. For example, due to its comparatively higher sensitivity, the technique is capable of detecting polymer degradation at a much earlier stage than the other spectroscopic techniques. In its most commonly used form i.e. CL curves of integral emissions, the data is easy to interpret and requires very little processing. Further, a built-in furnace in a typical CL spectroscope (Figure: 1.4) provides provision for quick and controlled pre-analytical ageing for a long-term degradation study, which significantly reduces

the analytical time and chances of contamination of a polymer [98, 99]. It is also expected that, since the analysis is conducted in molten state of the polymer, any irregularities that might arise due to physical factors, e.g. mobility of the relevant species across the sample, heterogeneous nature of the degradation phenomenon, would have been reduced [95, 96].

Despite all its advantages CL spectroscopy, partly due to relatively poor understanding of the phenomenon behind CL emissions in polymers, has not yet reached the status of a routine analytical tool in polymer laboratories. All that is known so-far about the CL emission from polymers entails that, a typical CL signal evolving from a degrading polymer represents a low intensity phosphorescence emission of visible light in blue-violet region. The energy of such emissions i.e. 290-340 kJ mol^{-1}, corresponds to the energy difference involved in transition between a triplet and singlet state of a carbonyl group. Various exothermic reactions that are capable of providing the surplus amount of energy required for the genesis of such triplet-state carbonyls include direct thermolysis of hydroperoxides, disproportionation of alkoxy radicals, and β-scission [40, 41]. A detailed and widely established mechanism proposed by Russell and Shard proposes that the triplet carbonyls are generated by the highly exothermic (460 kJ mol^{-1}) bimolecular termination of primary/secondary alkyl or peroxy radicals (Scheme: 1.19.). The reaction proceeds through an intermediate tetroxide to give an excited carbonyl, an alcohol and oxygen [100].

Although widely acclaimed, the Russell mechanism tends to oversimplify the nature of the phenomenon by focusing on one reaction only. Introduction of modern CL machines with wavelength filters has shown that total CL emission from an ageing polymer consists of bands at multiple wavelengths, possibly related to multiple chemical species generated by different chemical reactions. Experimental evidence in the contemporary literature also suggests the presence of multiple CL emission sources in a given CL spectrum of polyolefin. A temporal change in the nature of the CL existing species, although associated with the formation of secondary oxidation species in a molten PP formulation, does suggest that more the CL emission can be explain by more than one mechanisms [92, 95]. Further, existence of a direct relation between the availability of oxygen and intensity of CL signal, and the kinetic investigations of the phenomenon suggest hydroperoxides as key species involved in the phenomenon. Amidst this debate on the nature of CL emission, a comparatively new mechanism has been introduced, which suggests that emission of light from a degrading polymer occurs via a chemically induced

electron exchange luminescence (CIEEL), and hence, restarts the debate again [92, 95, 101]. In the light of the results of the current study, the mechanistic aspects of the phenomenon of CL in polymers will be discussed.

Additional scope that can be related to the current work is based on the fact that the work investigates the CL behaviour of a vast range of stabilised PP-based formulation. Unlike the major part of the CL based research where virgin PP has been the focus and the qualitative aspects i.e. emission spectra, were not the target, both the integral emissions and the temporal spectra are acquired [92, 95, 98, 99]. An assignment of the CL spectra informed with literature is for sure a useful addition scientific literature.

Scheme: 1. 19. Russell mechanism of chemiluminescence emission from polyolefin [90].

1.7.3. Analysis of the emissions from PP

Thermo-oxidative degradation of PP generates low molecular weight products of volatile and semi-volatile nature that belong to a wide range of functionalities and expand over a wide scale of concentration. Both the qualitative and quantitative aspects of the PP emissions vary in response to a number of factors that can affect the phenomenon of thermo-oxidative degradation in a polymeric matrix [50, 54, 55, 57, 59, 76, 102, 103]. A careful analysis of the compounds among the emissions requires an analytical method/technique that has a diverse detection range and high sensitivity, and can analyse the degradation products with minimum interference from any external factors [49]. Gas chromatographic analysis, preceded by solvent-free extraction (SFE), is one of the methods that has previously been used in the work of relevant scope [14, 50, 54, 57, 58, 76, 102-104]. Currently available with a range of sampling methods and a variety of detectors, GC can identify and quantify volatile and semi-volatile compounds with greater sensitivity and detection range. Selection of GC as a technique for the current work is supported

both by the nature of the samples to be analysed and contemporary research on emissions from polyolefin.

GC-FID and GC-MS are the most commonly used gas chromatographic systems that are generally used for the analysis of volatiles. An FID uses a flame ionisation detector to combust the components of a mixture that are initially separated by a GC. A GC-FID is more reproducible and repeatable than a MS detector and produces a more linear response. It is therefore, in general, a preferred choice for quantitative analysis of known samples. One primary requirement for GC-FID based analysis of a sample, which also acts as a limiting factor, is the requirement of standard reference materials. In the current study, the availability of reference materials was a challenge due to the sheer number of the unknowns, the method was therefore, rendered unsuitable for the study. Unlike GC-FID, a GC-MS works on the principle that organic compounds undergo fragmentation that is characteristic of their structure and can be used to identify the parent compound. Advances in mass spectrometric research and better spectral databases, it has become easier to identify unknown compounds. Although ideal as a qualitative tool, a GC-MS instrument is more precisely defined as a semi-quantitative technique. In an MS based spectrum, peak area is directly proportional to the total count of ions generated during ionization and fragmentation stages of a compound which, is affected by volatility and thermal lability of a compound. The multiple components that are involved in the process of generation of ions to their transfer to the detector and eventual detection, undergo changes in their efficiency due to voltage fluctuations, contamination, and side reactions [79, 105, 106]. In the current study, despite its limitations, GC-MS was preferred over GC-FID due to its suitability for unknown samples. The next challenge in the current study was the physical nature of the sample. The emissions/low molecular weight compounds in PP are found entrapped in the polymeric matrix. To be available for an analysis, they are required to be forced out of the samples without affecting the physiochemical properties of the material. In the relevant works, it is a common practice to heat the matrix above ambient temperature and trap the subsequently arising emissions for analysis. The use of the conventionally used liquid-solid extraction procedures is not ideal due to multiple disadvantages. Among the key disadvantages are the time consuming nature of the method, use of organic solvents and potential interferences caused by high extraction temperature etc. Both the temperature and the extraction solvent are likely to have a significant effect on the degradation phenomenon. Besides, it is hard to keep the system free of contamination and stop the low molecular degradation products of interest from escaping the liquid extract during GC. Masking of the volatile organic compounds with molecular weight less

than that of the solvent peak is an problem. Further, the low solubility of PP in most of the organic solvents makes solid-liquid extraction less suitable procedure for polymer analysis. SFE techniques address most of the issues encountered during a solid-liquid extraction; the SFE-based method entails a solvent free extraction followed by a direct analysis of the extracted emissions in significantly shorter time and with significantly reduced chances of contamination. Static headspace extraction (SHE), thermal desorption (TD) and solid-phase micro-extraction (SPME) are the techniques that have been widely used to study emissions from polyolefin [47, 49, 107, 108]. All three methods have their own advantages and disadvantages, which are reviewed in the rest of this section. The final selection of a method is, as much determined by its ability to address the set targets of a study, as by its cost effectiveness.

SHE for example, is the most commonly used tool in analytical laboratories. It is a fast, convenient and comparatively cost effective method for the analyse of volatile and semi-volatiles. Unlike the other two techniques i.e. TD and SPME, that have the additional enrichment factors provided by the adsorption phases, SHS is based on an unassisted accumulation of VOCs and SVOCs over the headspace of a sample sealed in a vial kept under a controlled set of experimental conditions. In the automated form of SHE, an aliquot of the sample headspace is transferred via a transfer loop to GC with the help of a carrier gas. It is important to mention that SHE only analyses a small portion of the sample headspace. The headspace is further diluted by the addition of the carrier gas causing a decrease in the method sensitivity. For the current work, an additional limiting factor arises from the limited availability of air inside a sealed vial that can be utilised during thermo-oxidative degradation of PP [48, 109].

TD and SPME are based on the use of an adsorption phase that has the ability to provide an enriched extract, and hence a higher sensitivity than a typical SHE method. SPME is relatively new technique that has gained significant importance for the extraction of volatiles from samples like air, food, water, soil and polymers [76, 110]. Currently, a given SPME analysis can be done both by a manual or automated method. A typical SPME device consists of a retractable fused silica fibre, coated with polymeric stationary phase housed in a specially designed holder. The fibre is directly exposed to a liquid sample or gaseous headspace over a liquid or solid sample. After the state of equilibrium is reached between the headspace the fibre, it is desorbed onto a GC inlet for desorption and subsequent analysis [111]. The commercially available SPME stationary-phase coatings include polydimethylsiloxane (PDMS), polyacrylate (PA),

divinylbenzene (DVB), and carboxen (CA). Choice of an SPME fibre for a particular sample depends on molecular weight and polarity of the sample. Although, the yield of the volatiles recovered by SPME is relatively smaller than the other methods, very low sample loss is observed. In contemporary work, SPME-GC-MS has been one of the main techniques used for the analysis of degradation products of polyolefin. The role of SPME, being a comparatively new technique, still seems somewhat unclear; in some studies the results are very promising, while in the others techniques is reported to be unable to show expected results. The apparent contradictions can be due to the experimental approaches that have been adopted; a dynamic extraction approaches, for example has been reported to show more promising results than a static design of experimental set up. While the use of an adsorption phase provides an additional factor of enrichment for extract in SPME and TD based extraction, as the adsorbents cannot be considered universal, it also introduces the selectivity factor.

Unlike SHS, TD makes use of an adsorbing agent to extract the volatile and semi-volatiles from a headspace. The sensitivity of this technique is reported to be significantly higher than SHS. Further, unlike SHS, the cost of adsorption tubes and requirement of the comparatively expensive TD unit, makes TD-GC-MS a more expensive method [14, 57].

Another technique known as Micro-scale sealed-vessel (MSSV) extraction was used to address the potential selectivity issue that might affect the TD and SPME based results. MSSV, an established extraction technique in geochemistry and petrochemicals, is comparatively a new in polymer analysis [112]. The current work, backed with only very little work that has already been done, will allow an evaluation of the technique for the degradation studies in polyolefin. In MSSV, the sample is sealed and aged in a pre-cleaned glass tube of specific dimension and for a predetermined period of time and temperature. The volatile organic compounds generated are analysed in a GC equipped with an MSSV-inlet [113, 114]. Although, like SHS, MSSV does not make use of an adsorbing agent, the sensitivity is significantly enhanced by the least loss of headspace that is transported to the GC-inlet under sealed conditions. For this particular work, MSSV is likely to be adopted with a view that it will have a complementary role for TD and SPME, where the selectivity of adsorption by the adsorbing agent might act as a limiting factor.

An important feature of analysis of the emissions during the current work was quantification of the volatiles. Attributing absolute numbers to emissions from polymers in TDS-GC–MS and SHS-GC– MS can be quite challenging. One approach is to calibrate via liquid injection. Using

this sample introduction system for calibration seems risky to us, as slightly differing flow characteristics in the different inlets (i.e. the TD and SHS inlet on the one hand and the liquid-injection inlet on the other hand) may result in differing discrimination effects. This jeopardizes the calibration via liquid injection. Introducing calibration solutions using the TDS and the SHS systems, one faces the problem that very small volumes of calibration solutions have to be transferred into TDS tubes and SHS vials. This implies dosage problems. To sort them out an internal standard can be used [16]. However, in order to add the internal standard to the SHS vial containing the polymeric sample the septum is usually pierced. In this way, leakage cannot be excluded. To use bigger volumes of highly diluted analyte-solutions is not an alternative; the solvent might clog the cryo-focussing system and disturb the equilibrium in SHS. Furthermore, the risk that analytes evaporate while preparing the calibration samples is high, especially for highly volatile analytes. Immobilizing the analytes on adsorptive material facilitates the dosage of small analyte amounts and reduces the risk of analyte loss without introducing big amounts of solvent into the sample-introduction system. However, if analytes are not fully desorbed inaccurate calibration curves will be acquired. In view of these difficulties, only comparative studies were performed in the current work. Nevertheless, future studies will focus on the task of absolute quantification as well [103].

CHAPTER: 2. EXPERIMENTAL

2.1. Materials

2.1.1. Polypropylene

All PP formulations investigated in the current study were made using a homopolymer. PP, Grad: 5014PD (Z/N, slurry), was purchased from Korea Petrochemical Industries. The polymer was singly extruded on a twin-screw extruder in presence of nitrogen as the extrusion medium, using the same method (Section: 2.1.3). The samples extruded into pellets were analysed without any further treatment. In the current report, due to secrecy agreement with the sample provider and the financial sponsor, only the information on the types of additives and their order of mixing is provided, while the exact ratio of the components in the formulations is not disclosed.

2.1.2. Additives

The current study is based on the analysis of PP degradation in stabilised form of the polymer. The selection of the stabilisers/additives and their subsequent combination into stabilisation packages was therefore, an important step. The key groups of antioxidants commonly used for PP stabilisation include organophosphites, hindered phenols, thioesters and hydroxylamines. There is also an increasing trend of utilising natural antioxidants like vitamin E as polyolefin stabilisers. The antioxidants that were used in the current study include an organic phosphite (SN1680), two hindered phenols (SN1010 and GA-80), two thioesters (DSTDP and SN4120), a light stabiliser (SL1190), a hydroxylamine (FS042) and vitamin E. The full names and the corresponding commercials identification codes for the antioxidants are given in the Table: 2.1, while their physical properties and chemical structures are given in the Table: 2.2 and Figure: 2.1, respectively. In addition to the above mentioned antioxidants, each formulation (except the formulation N, which had ZnO) had SC-110 as an antiacid.

The choice of the stabilisers/additives was made after literature search and consultation of the academic and industrial experts in the supervisory committee of the project. The additives were provided by Songwon Industrial.

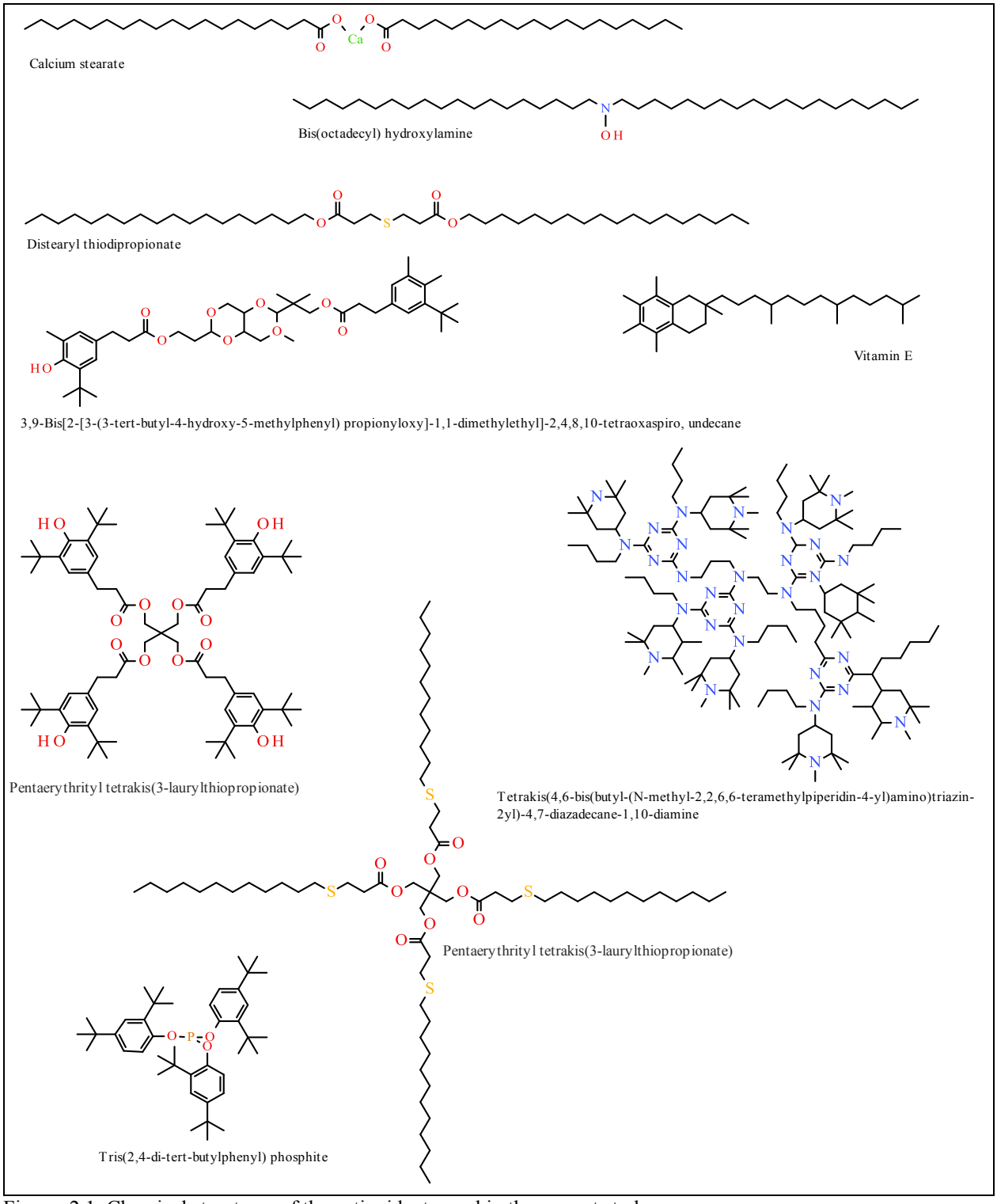


Figure: 2.1. Chemical structures of the antioxidants used in the current study.

Table: 2.1. Chemical names and corresponding commercial I.Ds for the additives used in the current study.

Chemical Name of the additive	I.ds
Calcium stearate	CaSt
Zinc Oxide	ZnO
Tris (2,4-di-tert-butylphenyl) phosphite	SN1680
Pentaerythritol tetrakis (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	SN1010
3,9-Bis [2-[3-(3-tert-butyl-4-hydroxy-5-methylphenyl) propionyloxy]-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro, undecane	GA-80
Distearyl thiodipropionate	DSTDP
Pentaerythrityl tetrakis (3-laurylthiopropionate)	SN4120
Bis (octadecyl) hydroxylamine	FS042
Tetrakis(4,6-bis(butyl-(N-methyl-2,2,6,6-teramethylpiperidin-4-yl)amino)triazin-2yl)-4,7-diazadecane-1,10-diamine	SL1190

Table: 2.2. Physiochemical properties of the additives used in the current study

I.Ds	Molecular Weight	Melting point
CaSt	607	155°C
ZnO	81	1975°C
SN1680	646	187°C
SN1010	1177	115-118°C
GA-80	740	110°C
DSTDP	683	65-67°C
SN4120	1161	48-54°C
FS042	537	96-99°C
SL1190	2285	146-150°C

2.1.3. Combination of the stabilisers/additives into stabilisation packages

Stabilisation packages in real life PP-based formulations are typically multi-component systems. They comprise of a combination of stabilisers to provide protection from degradation during processing and service life of the polymer. While the processing stabilisers are mainly aimed at protection from thermal, mechanical and oxidative degradation, the service life stabilisation packages also require light stabilisers. The selection of service life additives is also determined by the end-use applications of the polymer. Each of the stabilisers in the current study was selected due to the peculiar role they are known to play in controlling PP degradation at various stages of the life cycle of the polymer. Organophosphite and hydroxylamines, for example, are established processing stabilisers, while hindered phenols control degradation during processing as well as during service life of a polymer. The hindered phenols are also known for their synergy with organophosphites. Similarly, thioesters are used as service life stabilisers for high temperature applications and have been known for their synergy with hindered phenols.

Although each group of PP stabilisers/antioxidants is known to follow a generic stabilisation mechanism, structural variations among the individual members of a group can cause significance difference. The stabilisation mechanism of an antioxidant is also affected by the nature and physiochemical properties as well as concentration of any other stabilisers present in a given formulation. The cumulative stabilisation effect of a given stabilisation package is, therefore, anything but a simple sum of the individual stabilisation routes of the antioxidants in a given package. To address this aspect of PP stabilisation, the stabilisers/additives have been systematically mixed to reveal the nature of the interactions among them (Table: 2.3-2.5). The PP formulations prepared for the current study can be divided into three different groups:

- The first set of the formulations or the Group: 1, comprised of seven different combinations of stabilisers. The combinations designated by sample identification: A-G are shown in the Table: 2.3. The stabiliser combinations in this group were aimed at hindered phenol (SN1010 and GA-80) and thioester (DSTDP and SN4120) groups of antioxidants. In all formulations of the Group: 1, an organophosphate (SN1680) was used as a processing stabiliser, while CaSt as an antiacid. The combinations in this group have previously been investigated for their performance in polymer stabilisation. They are also commonly used combinations in commercial applications, both due to cost effectiveness and optimum performance required for a wide range of PP applications.

- The formulations in the second group/Group: 2, designated by sample identification: H-L are shown in the Table: 2.4. This group had the organophosphite (SN1680) replaced with a hydroxylamine (FS042). Hydroxylamine is another processing stabilisers, but relatively less commonly used. The aim was to investigate the effect of this change on the hindered phenol and thioester combinations already explored in the Group: 1 samples.

- The third group of the formulations, as shown in the Table: 2.5 included more unique compositions. The sample ‘M’, for example, had a natural antioxidant incorporated in it, while in the formulation ‘N’ CaSt was replaced with ZnO. Similarly, in the formulation ‘O’ a light stabiliser SL1190 was used. All formulations of this group i.e. M-O, had the antioxidants combination that have not previously been investigated, especially for emissions. In that aspect, it gave a novel feature to the current study.

The synthetic, processing and analytical features, other than composition of the samples, were kept the same. The changes in their physiochemical behaviour during the experimental conditions therefore, could be related to the composition of the stabilisation packages.

2.1.4. Compounding of the PP formulations

The stabiliser/additive combinations described in the Section: 2.1.3, were dry mixed with PP and compounded using a twin-screw extruder. Compounding is the process of mixing additives and a polymeric matrix under mechanical friction and heat effect. The polymer and the additives, pre-mixed by physical means, are introduced into the extruder melts. While passing through the hot extruder zones the molten mixture undergoes mixing between heated moving screws of the extruder. Extrusion can be adapted to be conducted under different experimental conditions, e.g. under vacuum, in presence of oxygen or nitrogen. Similarly, the temperature of different heating zones and the rotation of the extruders can also be changed as suitable for a given polymer. After hot-mixing, the molten mixture is finally introduced into a cold-water trough placed adjacent to the outlet of the extruder where it solidifies into polymer threads/fibres. The fibres are eventually chopped into cross-sectional shapes/pellets on a die.

For the current work, compounding was done using a Thermo-Prism TSE HC24 modular twin-screw extruder fitted with a Brabender gravimetric feeder (Figure: 2.2). A dry-blended mixture of the raw polymer and additives was introduced into the extruder through the ‘hopper’ where it was melted. The molten mass was mixed between the screws rotating at a speed of 300 rpm. The temperature profile of the extruder zones was set in the range of 190-215°C (Figure: 2.2). In order to reduce the effect of processing parameters i.e. temperature and oxygen, the extrusion was conducted only once, while nitrogen was used as the extrusion medium. The samples were stored at ambient in dark place packed in brown bags until the time of analysis. The additives that were supplied were sent in PP bottles and were also stored at ambient in dark place. For any experimental work the samples were directly taken off the packaging to reduce the effect of direct UV exposure.

Table: 2.3. PP formulations Group: 1 (stabilised with a organophosphate, hindered phenols and thioesters).

Sample I.D		A	B	C	D	E	F	G
Polymer	PP	■	■	■	■	■	■	■
Additives	SC-110	■	■	■	■	■	■	■
	SN1680	■	■	■	■	■	■	■
	SN1010		■		■		■	
	DSTDP				■	■		
	GA-80			■		■		■
	SN4120						■	■

Table: 2.4. PP formulations Group: 2 (stabilised with hindered phenols, thioesters and a hydroxylamine).

Sample I.D.		H	I	J	K	L
Polymer	PP	■	■	■	■	■
Additives	SC-110	■	■	■	■	■
	FS042	■	■	■	■	■
	SN1010		■	■	■	
	DSTDP			■		
	GA-80					■
	SN4120				■	■

Table: 2.5. PP formulations Group: 3.

Sample I.D		M	N	O
Polymer	PP	■	■	■
Additives	SC-110	■		■
	SN1680			■
	SN1010	■		
	DSTDP	■		
	SL1190			■
	SN4120		■	
	Vitamin E	■		
	ZnO		■	

2.2. Equipment/Instrumentation

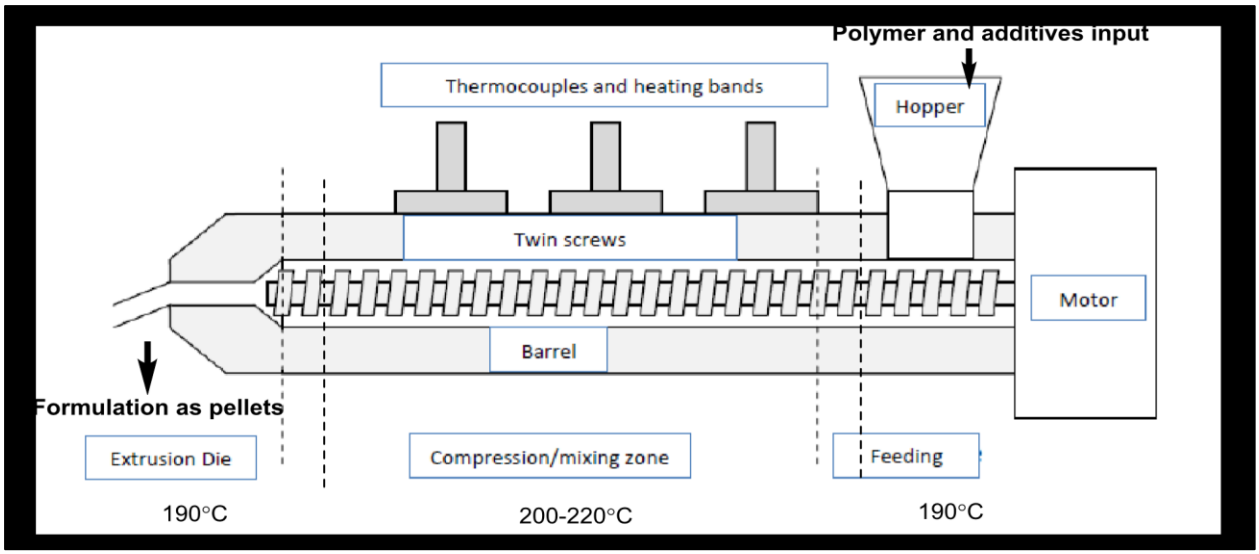


Figure: 2.2. A schematic of a typical twin-screw extruder.

PP formulations were compounded using a Thermo-Prism TSE HC24 modular twin-screw extruder fitted with a Brabender gravimetric feeder. The samples thus prepared were tested by IR and CL spectroscopy, and GC-MS methods for the emissions from them. For the IR analysis, the samples were aged in aluminium containers in a conventional laboratory oven. The IR analysis was done on a Nicolet iS5 FATR-TIR Spectrometer fitted with iD5 Diamond ATR (Figure: 2.3). CL analysis was done using an ultra-high sensitive CLA-FS3 spectrophotometer (Figure: 2.4).

Headspace analysis of PP emissions was done using an E7694 auto-sampler connected with a Agilent 7890A GC hyphenated with a 5975 mass spectrometer. Glass headspace vials (20 ml) with aluminium crimp-caps and PFTE septa were used for sampling, while GC separation was done on a DB-5 column (30 m x 0.25 mm). Thermal desorption sampling was done on Tenex tubes, while a Merck thermal desorption unit connected with a 6890N, 5973 was used for this method.

SPME-GC-MS analysis was done using a 6890 CG hyphenated with an MD 900 mass spectrometer. An SPME specific GC liner, from Sigma Aldrich, was used for increased GC-MS method sensitivity. GC separation was done on a DB-5 column (30 m x 0.25 mm). The four different types of SPME fibres used in the current study (PDMS, CAR/PDMS, DVB/PDMS,

CAR/PDMS/DVB) along with a manual holder assembly were also purchased form Sigma Aldrich. The headspace vials used for static headspace sampling (20 ml) were the same as used in the headspace GC-MS method.

For the static SPME-GC-MS method, a 1.5 L steel chamber closed with a lid and sealed with a silicon seal was used (Figure: 3.9). Dynamic SPME-GC-MS analysis was conducted in a purpose built thermal desorption unit. In the thermal desorption unit, sampling was done in replaceable glass tube of 7.8 cm length and an internal diameter of 4 mm. The details of the unit are given in the Section: 2.3.3.1c and the stricture is explained in the Figure: 2.6.

MSSV-GC-MS analysis was done on a 6890 GC hyphenated with an MD 900 mass spectrometer. The liner of the GC system was adapted for MSSV sampling by replacing the glass liner with a purpose made steel tube of dimensions 7.5 mm x 0.25 mm (Figure: 2.7). The liner/metal tube was fitted with a metal plunger. The polymeric sample for the MSSV-GC-MS analysis was prepared in small glass tubes. Each tube was 30-40 µl in internal volume and was bent at an angle of 120°, for ease in cracking inside the GC liner.

2.3. Methods

2.3.1. Attenuated Total Reflectance Infrared Spectroscopy

ATR-IR analysis of thermo-oxidative degradation of PP was conducted on PP pellets. Prior to IR scanning, the samples were aged in conventional laboratory oven in aluminium dishes. While exposed to ageing temperature in the oven, the aluminium containers were kept covered with aluminium foil to avoid cross-contamination. Each of the fifteen formulations were aged at 90°C, 120°C and 150°C over a period of 20 hrs. After every 1 hr interval of ageing, each sample was scanned for IR spectra.

Before analysing a sample, the ATR sample window was clean-dried with acetone and an air-blank was acquired. The air-blank was necessary as the presence of air in the spaces between the sample and the ATR window cannot be completely avoided. A sample-blank was run by pressing an un-stabilised PP (powder) between the ATR-arm and the ATR-window, and scanning it using the same IR method as for the stabilised PP formulations. Each of the PP

formulation was tested by placing a PP pellet between the ATR-arm and the ATR-window of the instrument, and scanning it by the method described below. The IR data was saved in asv. files and plotted in excel to be included in the current report. The main IR region that has relevance for PP degradation is 600-4000 cm^{-1}, it is therefore, only that region which is reported in the IR spectra included in the current report (Section: 3.1 and Chapter: 4).

Figure: 2.3. An ATR-IR instrument.

The ATR-IR analysis of the blank and the samples was done for a frequency of 500-4500 cm^{-1} at a scan rate of 4 scans/second. Each sample was tested in triplicates, and the data was plotted as average of the triplicates. Peak assignment was done by comparing the spectra with contemporary research literature. To elaborate on the quantitative aspects of the data, a group of peaks (corresponding to carbonyls) were selected to measure carbonyl indices of the samples. The carbonyl indices were calculated by dividing the peak height of carbonyl peaks (1500-1700 cm^{-1}) with that of the reference peaks i.e. 1450 cm^{-1} and 1374 cm^{-1}. The indices plotted against time gave an alternative view of the degradation behaviour of the polymer over time.

2.3.2. Chemiluminescence spectroscopy

The same PP formulations that were analysed using ART-IR method were also tested by CL spectroscopy. An ultra-high sensitive CLA-FS3 model CL spectrophotometer was used for the

analysis (Figure: 2.4). The detectors in the spectrophotometer are photomultiplier tubes working for a wavelength range of 300-850 nm. Unlike IR analysis that involved ageing of the samples prior to their analysis, the CL spectroscopic analysis involved simultaneous ageing of the samples, and detection/measurement of the subsequently generated emissions. The polymeric samples, in the current study, were aged in the furnace installed inside the spectrophotometer. The furnace was equipped with thermal and pneumatic controls allowing sample degradation at a range of thermal conditions, and in presence of various ageing environments, e.g. nitrogen, air and vacuum etc. For each of the fifteen formulations in the current study, a 0.5 mg of the sample was placed in a stainless steel dish and aged at 200˚C in presence of oxygen at a flow rate of 50 ml min^{-1}. The selection of high ageing temperature, and oxidation environment was made to allow high CL emissions. Further, analysing the polymer in molten meant reducing complication that could have generated due to irregularities in the physical features of the polymer. The emissions from the samples were recorded in qualitative as well as quantitative mode, commonly known as CL emission spectra and integral CL emission, respectively.

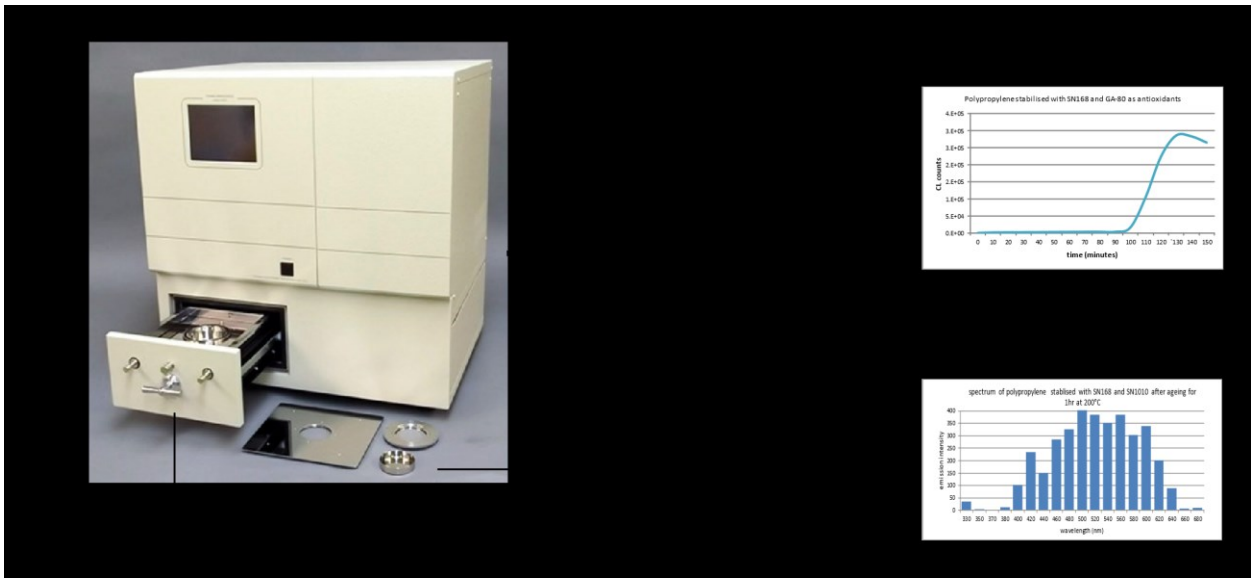


Figure: 2.4. A chemiluminescence spectrophotometer and typical CL data.

Unlike UV-Visible and IR spectroscopic methods, the CL analysis required a pre-accumulation of CL emitting species for an amplified CL signal. In the current study, the accumulation time for the CL emitting species was 10 min, which was selected based on the contemporary literature and after advice from technical experts. The emissions recorded at every 10 min interval were plotted against time, generating a so-called integral CL emissions curve (Figure: 2.5). Every point in the curve represented a change in the intensity of the CL-active species when compared

with the previous point. For each PP formulation the CL emission scanning was continued until the CL signal attained a stable intensity, or at least reached a maximum.

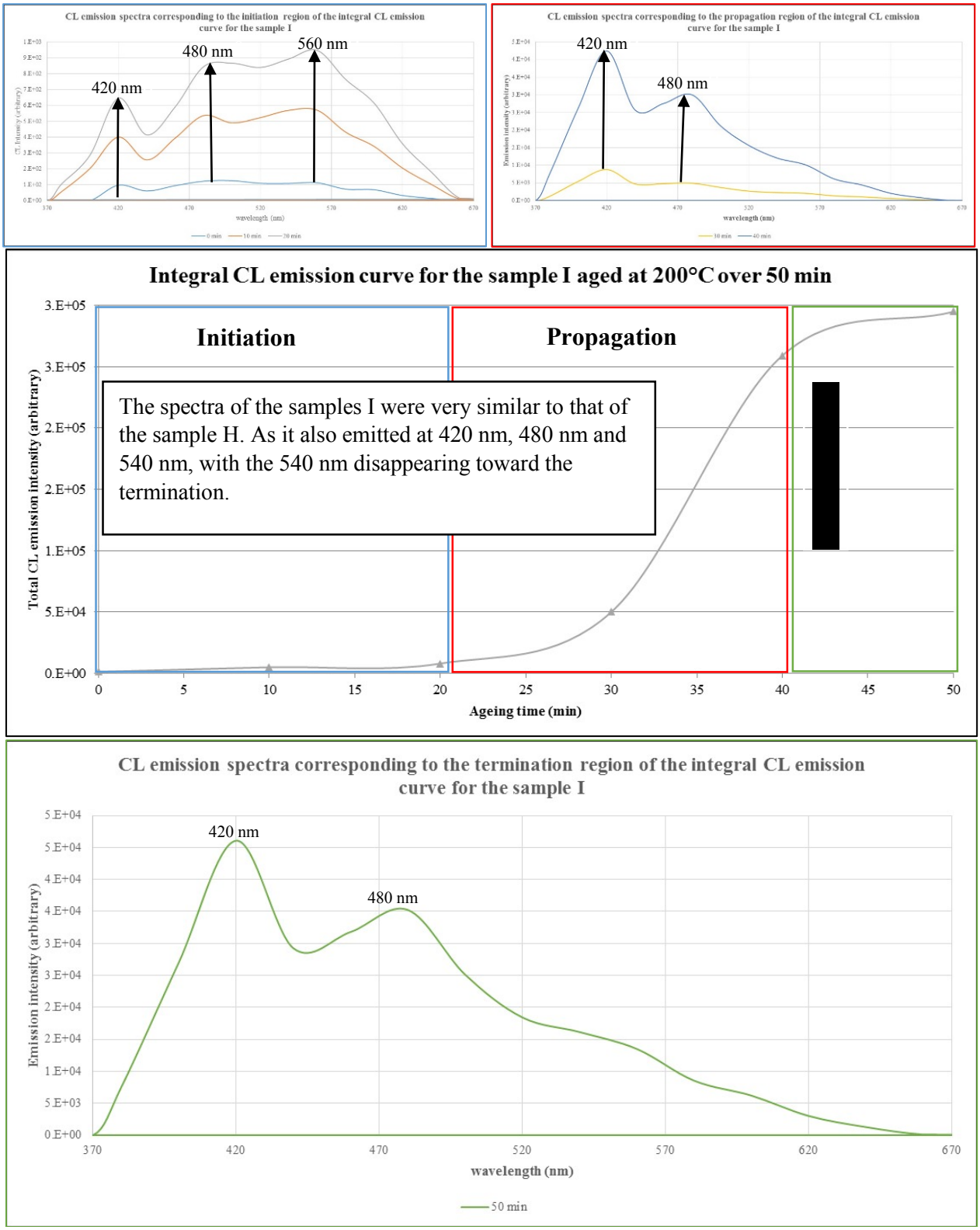


Figure: 2.5. Integral CL emission and corresponding spectra for the formulation I (Table: 2.4).

The integral CL emissions for each point on an integral CL curve were resolved into individual bands by 20 different wavelength cut-filters in the instrument. The spectra thus acquired had CL emissions intensity plotted against wavelength over a range of 300-700 nm. The integral curve and spectra data for the CL emissions was recorded to investigate the thermo-oxidative degradation chemistry in molten state of stabilised PP formulations (Figure: 2.5).

2.3.3. Chromatographic methods

The chromatographic analysis of the emissions from PP required the emissions trapped and transferred to a GC-MS system. The trapping can be done using different headspace methods. In the current study, the initial headspace sampling was done using four different headspace methods. The multiple methods were used as a part of method optimisation and selection of the most appropriate method for the final testing. Details of the GC, the MS, and the sampling methods are included in the rest of the current section. The various chromatographic methods that have been used during the current study i.e. in the HS-GC-MS, TD-GC-MS, SPME-GC-MS and SPME-GC-MS, varied mainly in the sampling/extraction stage of analysis while the separation and detection stages varied only slightly.

In the GC method, after initial method optimisation, a 30 m non-polar capillary column was used throughout the project. With the exception of the TD-GC-MS method (see Section: 2.3.3.1b), the oven programme was set for 30-310˚C at a ramp rate of 8˚C min^{-1} with the initial and final held times of 2 min and 10 min, respectively. Except for the MSSV-GC-MS method (Section: 2.3.3.1d), sample injection was done in splitless/split mode. The sample stream was left splitless for initial 2 min, followed by a split mode for the rest of the method. The inlet liners for SPME and MSSV methods were also specific for the methods. The former made use of SPME specific Sigma Aldrich liner, while the latter utilised a metallic liner that was designed at GC^2 (Section: 2.3.3.1c-2.3.3.1d).

A standard mixture of hydrocarbon (C12-C32) in hexane has been used to optimize the GC-method, and was used to evaluate the condition of the column at regular intervals during the span of the experimental work. Prior to any testing, the GC column was conditioned at 310°C to get rid of any column bleeds. A column and process blank was done between the samples, to avoid any cross-contamination.

2.3.3.1. Headspace sampling methods

2.3.3.1a. Static headspace extraction

Static headspace extraction of the PP emissions, for a subsequent GC-MS analysis, was conducted using E7694 headspace auto-sampler connected to an Agilent GC-MS (7890A/5975C). For each test, an accurately weighted 2 g of the polymer sample was sealed in a 10 ml headspace vial from Crawford Ltd. The sample was aged inside the headspace oven at 150˚C for 2 hr. After an equilibration 1 min an aliquot of the sample headspace was transferred to the GC inlet via a silicon transfer-tube. Argon was used to transport the headspace across the transfer line. After testing different pressures, 13 psi was found to be the optimum pressure for Argon. A blank vial was set between the test-vials to clean the trace any contamination between the samples. The blank consisted of an empty vial that was aged under the same experimental conditions as the test vial.

2.3.3.1b. Thermal desorption/extraction

Thermal desorption of the emission from PP was carried out on a Marker TD unit using Tenax adsorption tubes. The unit was connected to a GC-FID and was operated in an automated mode. Toluene and hexadecane were used as standard reference materials for quantification of the VOCs and SVOCs, respectively. In the actual experiment, a thermal desorption tube was adsorbed onto pre-weighed (30 mg) polymeric material placed in a specially designed adsorption unit. The ageing/adsorption time and temperature parameters were set according to the VDA-278 protocol. The method is a standard protocol of vehicle development authority, for the measurement of emissions form plastics. The adsorption for this method was conducted at 90˚C and 120°C for a period of 30 min and 60 min for the analysis of volatile and semi-volatile organic compounds, respectively. Contaminants were avoided by running blank runs on the pre-cleaned and conditioned thermal desorption tubes that were used for extraction. Separate, disposable tubes were used for each sample, to avoid cross contamination among the samples. The data acquired was processed through automatic peak integration and was reported as total emissions for the respective samples.

2.3.3.1c. Solid-phase micro-extraction

After initial experiments with conventional static SPME method commonly described in the literature on polyolefin emissions, which did not prove very successful, a dynamic SPME

adsorption unit was assembled for the current study (Figure: 2.6). The unit consisted of a cartridge heater with a replaceable glass-lining. The rear of the tube (sample housing) was thermally controllable from ambient to 500˚C, while its back stayed at ambient temperature (SPME fibre-housing). The sample was swapped with air while it was aged at a given temperature for a predetermined period. Air was used to facilitate thermo-oxidative degradation of the polymer as well as flow of the sample emissions situated at the other end of the sample tube, counter-clockwise to the air-current. To avoid contamination caused by surrounding environment and any contaminants inside the adsorption unit, process-blanks and fibre-blanks were run regularly. For the fibre-blank, the SPME fibre was desorbed in the GC-liner at 300ºC for 10 min. The cleaned fibre was then analysed to make sure that it is free of any contaminants. Any possibility of contamination from the adsorption unit was tested by running a blank on the fibre under the experimental conditions without any sample inside the tube.

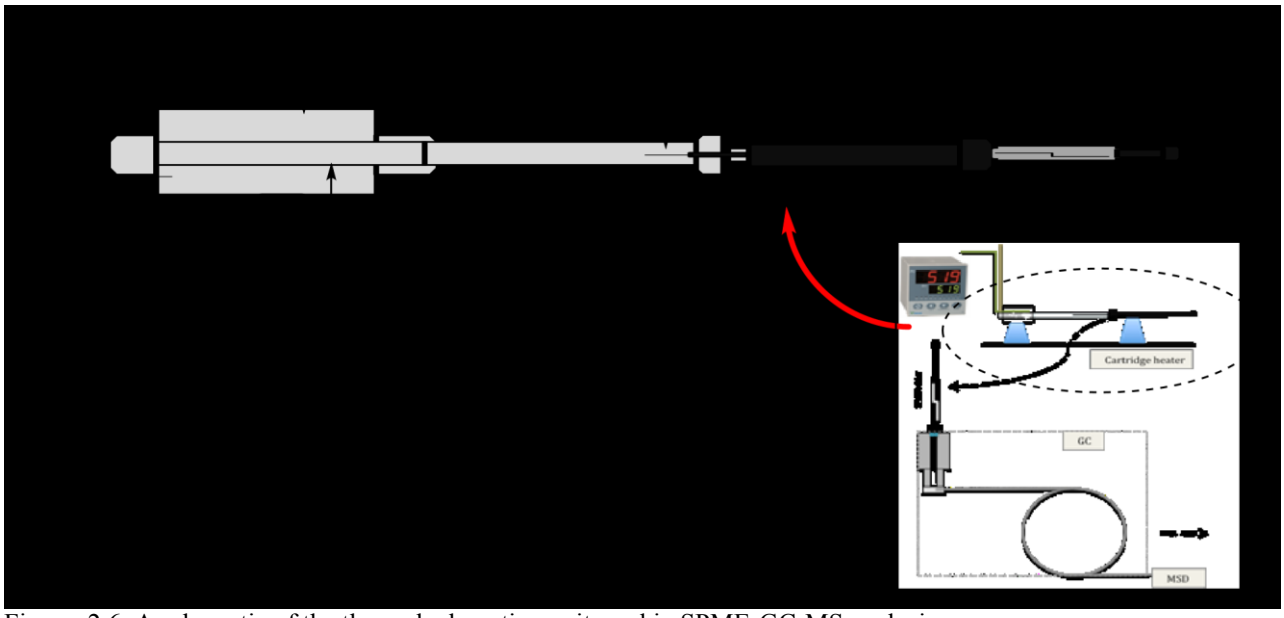


Figure: 2.6. A schematic of the thermal adsorption unit used in SPME-GC-MS analysis.

2.3.3.1d. Micro-scale sealed-vessel extraction

A schematic of MSSV-GC-MS instrument, which was developed after modification of the conventional GC-liner, is shown in the Figure: 2.7. A typical MSSV extraction involved ageing of the sample in a MSSV tube followed by the release of the trapped headspace into the GC inlet.

For a test, 20 mg of the sample was carefully filled and sealed in a pre-cleaned micro-vessel of glass. The sample inside the vessel was then aged in a conventional laboratory oven at 150˚C for a period of 24 hrs. For the GC-MS analysis the sealed vessel, with aged sample and subsequently generated headspace, was placed inside the GC inlet, purpose adapted for MSSV-GC-MS analysis. As shown in the Figure: 2.7, the MSSV inlet port consisted of a metallic tube equipped with a metallic plunger for cracking the tube when required. Before cracking the tube, the inlet port was purged with helium to get rid of any residual air or contaminants coming along the tube or other experimental equipment, e.g. callipers etc. Once the tube was cracked, any emissions released were cryo-focused before separation on a GC column and subsequent detection on an MS detector.

A HP-GC-MS instrument was used in all MSSV GC-MS work. MS was tuned for PFTA peaks at m/z value of 69, 208 and 205; any leaks were checked by comparing the peaks for water and nitrogen in the tune window. The GC column was calibrated using hydrocarbon mixture (C12-C32) in hexane. The method-blank for MSSV-GC-MS was prepared by sealing and ageing an empty MSSV tube prior to GC-MS analysis of its headspace by the same method as for a sample.

2.3.4. Mass spectrometric method

An MD 800 mass spectrometer was used in electron ionization mode for all experiments involving GC-MS work. Throughout the work, the ion source was set at a potential difference of 70eV. The mass spectrometer was set on a full scan mode for the m/z: 35-500. The instrument was manually tuned using perfluorotetradecanoic acid (PFTA) for the peaks at m/z: 69, 212 and 502 (Figure: 2.8). The selected masses represent stable fragments formed by PFTA, and are commonly used as standard group of fragments for MS tuning.

Mass spectra were acquired and processed on Chemstation for the SHS work, while MassLynx was used for the rest of the work. NIST and Wiley libraries of mass spectrometric databases were used for identification of the unknown peaks.

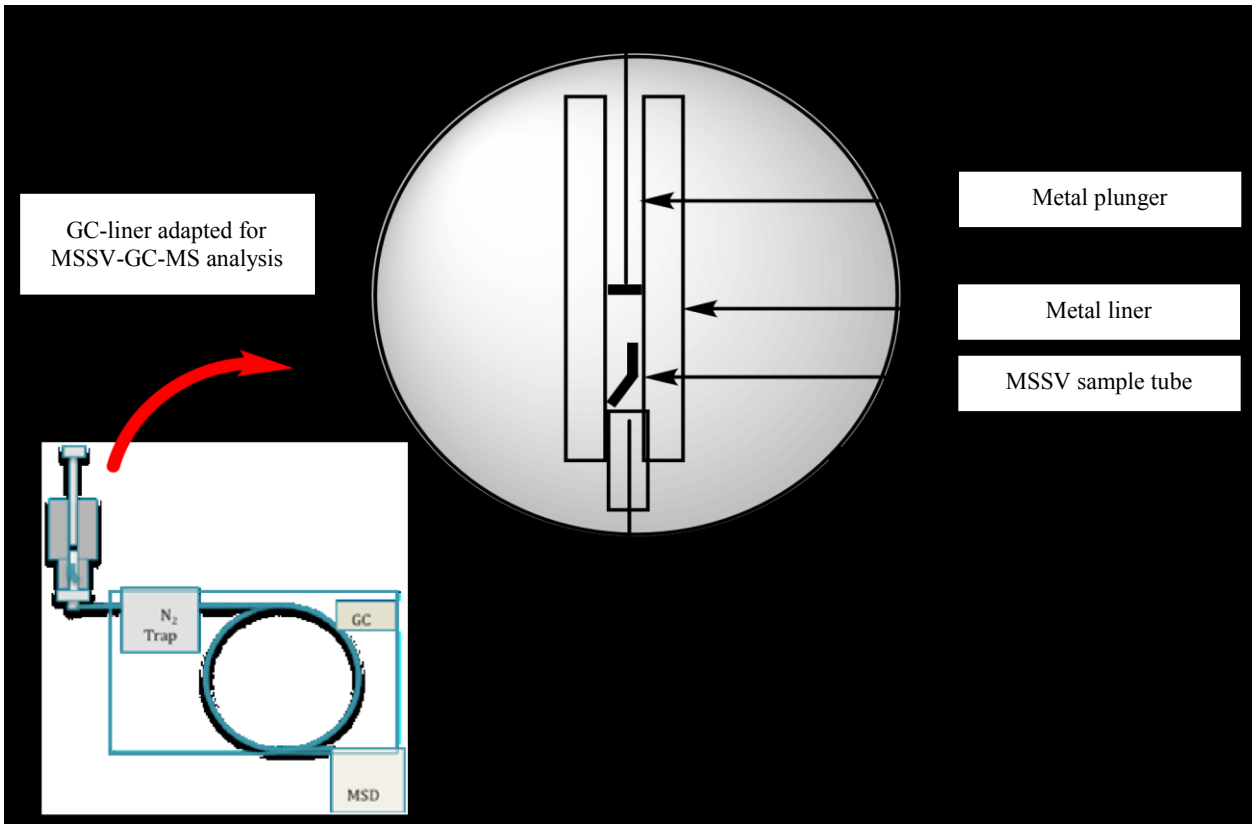


Figure: 2.7. A schematic of the MSSV-GC-MS set-up [113].

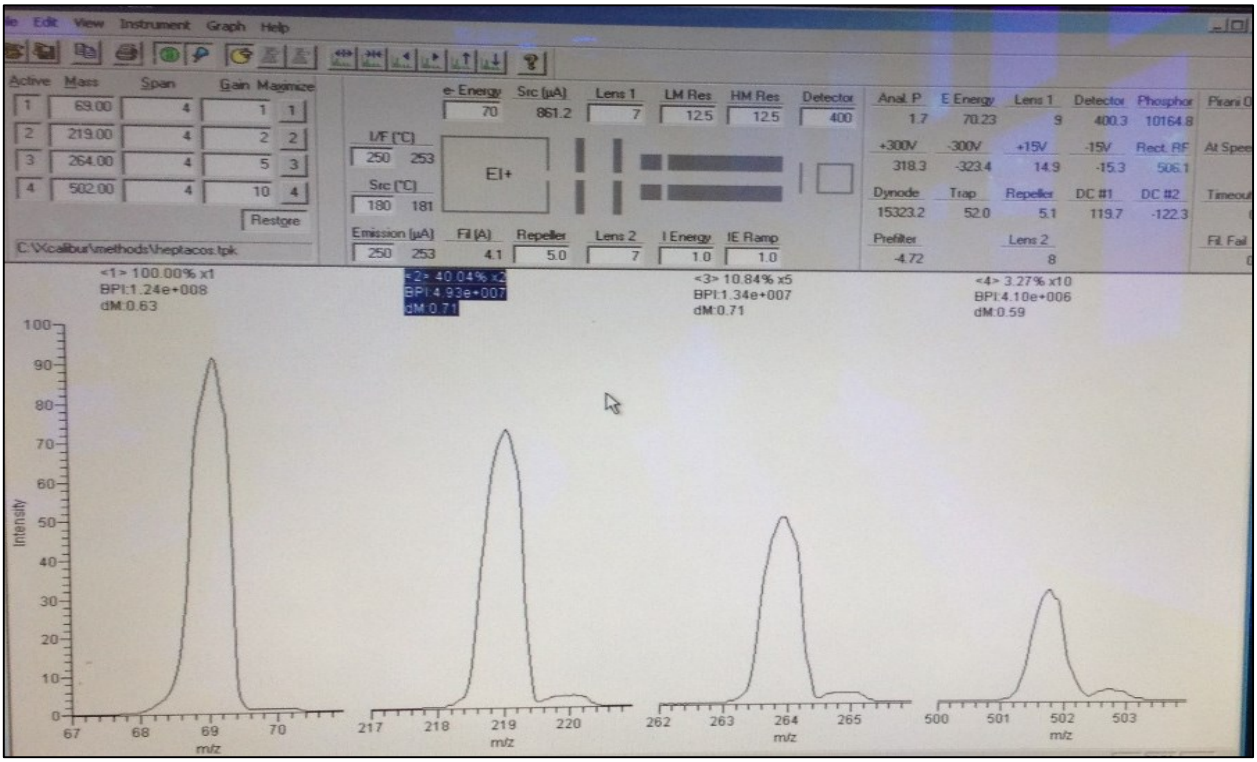


Figure: 2.8. A screenshot of the tune parameters used for the MS method.

CHAPTER: 3. METHOD DEVELOPMENT

The spectroscopic and chromatographic methods used for the analysis of degradation products in solid-state polymer and in the headspace of the polymeric formulations respectively, were carefully optimised for the range of important parameters that can affect the authenticity of the results. The method development indeed involved a significant amount of experimental work that needs to be described in detail before discussing the data acquired with the respective techniques. The three main sections that form the current chapter comprise of the method development work done for the ATR-IR spectroscopic (Section: 3.1), CL spectroscopic (Section: 3.2), and gas chromatographic work (Section: 3.3). While the ATR-IR and CL sections are relatively short, the GC-MS work is further divided into GC (3.3.1), MS (3.3.2) headspace sampling (3.3.3) and data interpretation sections.

3.1. ATR-IR method

ATR-IR analysis of PP degradation was conducted by exposing the pre-aged PP pellets to an IR-beam on the ATR-stage. The method is based on scanning the change in the relative proportion of any chemical species inside the matrix as it ages (Figure: 3.1). Although multiple products are generated during degradation of PP carbonyls are the primary products of PP oxidation and hence are of primary interest while studying thermo-oxidative degradation (Section: 1.4). One way to analyse carbonyls in a degrading polymer is to scan it for the presence of any carbonyl absorption/transmittance. Any temporal and thermal variations in the intensity/peak area of the carbonyl peaks can provide useful information about the degradation behaviour of the polymer. Typically, area/intensity of the IR peak corresponding to carbonyls is divided by that of an internal standard, the term thus obtained is called carbonyl index. The carbonyl indices measured at various intervals of time plotted against time give curves representing progress of thermo-oxidative degradation in a polymer [45].

The multiple peaks that can be used as an internal standard include 840 cm^{-1}, 1166 cm^{-1}, 1455 cm^{-1} and 2720 cm^{-1} (Figure: 3.3). The first two of the four peaks are sensitive to physical parameters, e.g. crystallinity of the material, while the third is susceptible to an overlap with the neighbouring peaks (Figure: 3.2. and 3.3.).

The peak at 2720 cm^{-1} however, showed stable intensity and chemical purity (Figure: 3.3 and 3.4). It was therefore, selected as the IS to calculate carbonyl index in the current study. To make the data more relevant to the emissions tests, the ageing for IR analysis was also conducted at 150°C and for a period of 20 hrs. Cross contaminations during oven-ageing was avoided by conducting the ageing in aluminium containers that were covered with aluminium foil.

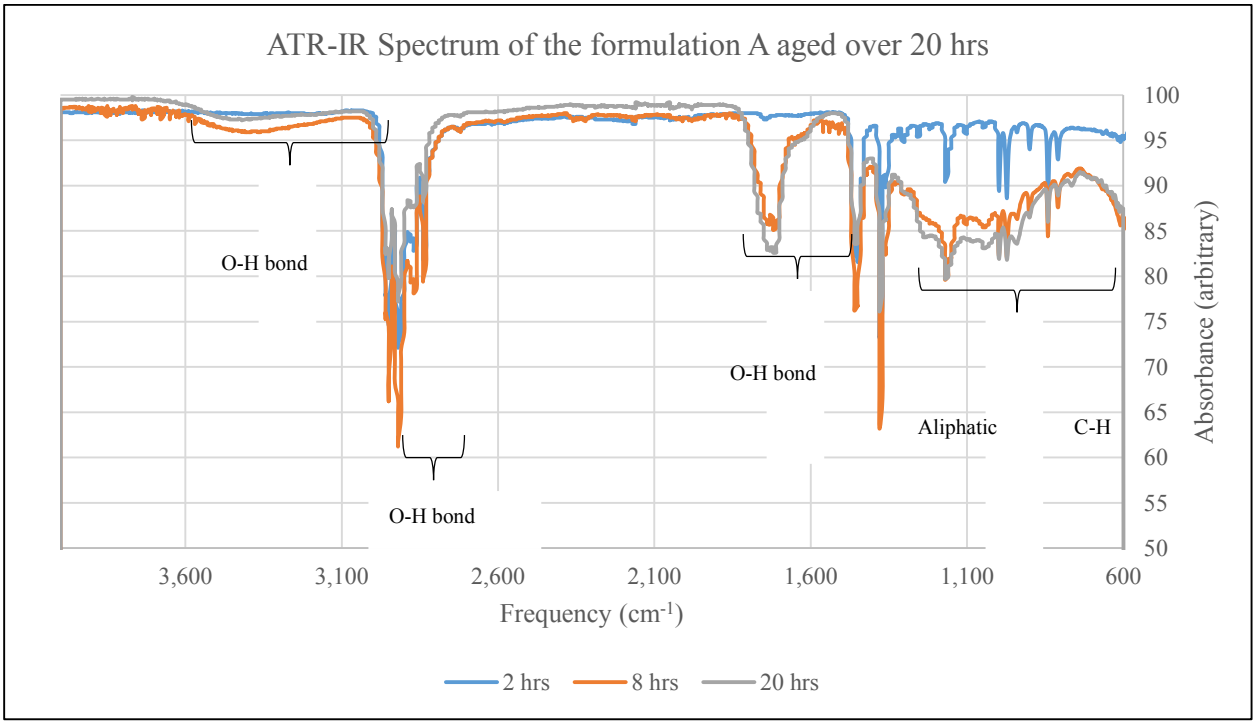


Figure: 3.1. ATR-IR Spectrum of the sample A aged (Table: 2.3) at 150°C.

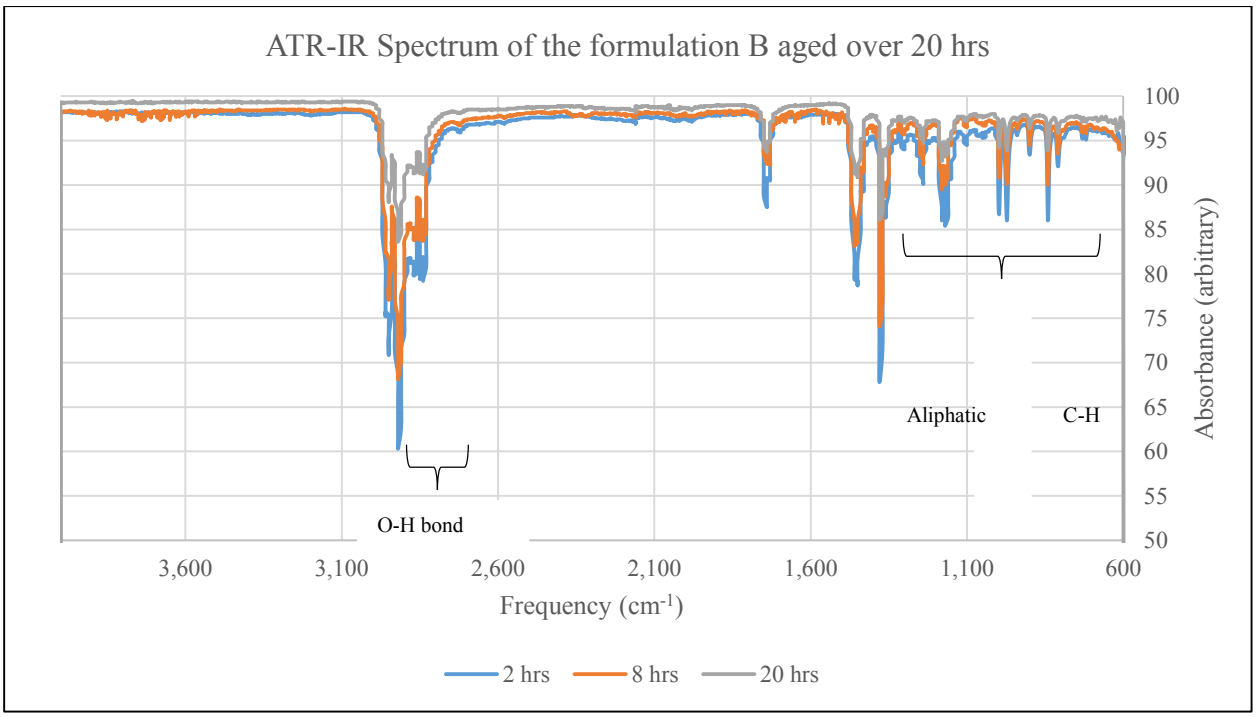


Figure: 3.2. ATR-IR spectrum of the sample B (Table: 2.3) aged at 150°C.

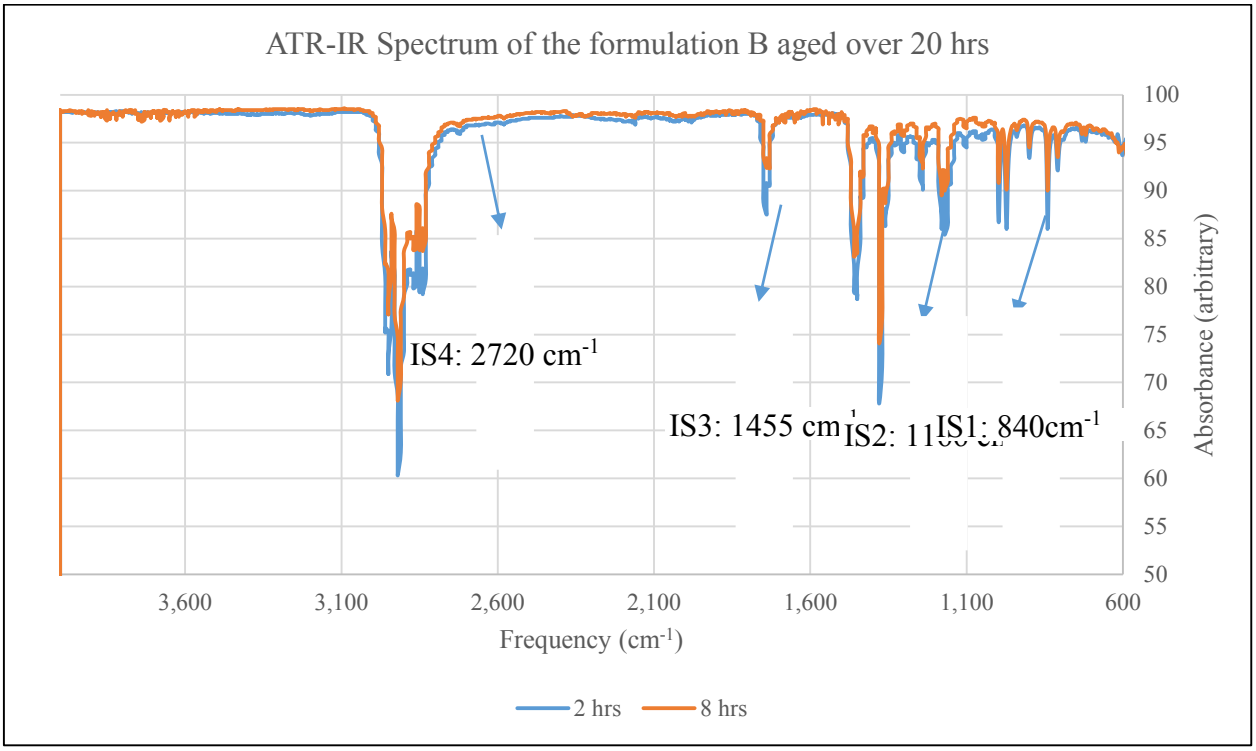


Figure: 3.3. Typical IR peaks used as internal standards for measurement of carbonyl indices for PP.

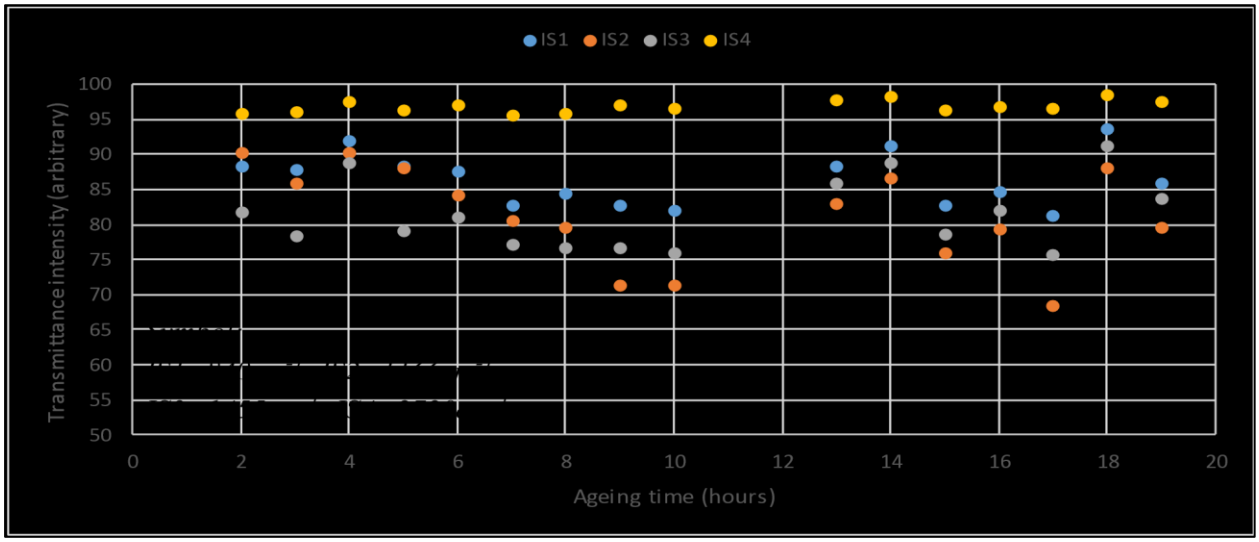


Figure: 3.4. Temporal variation in the intensity of the IR spectral peaks used as IS for PP.

Other than CIs, which are based on the total intensity of all carbonyl peaks, the nature of the individual carbonyls and the corresponding peak area/intensity are also a useful source of information on the progress of thermo-oxidative degradation in a polymeric matrix. Therefore, the peak assignment was also given due consideration in the current study.

3.2. Chemiluminescence spectroscopic method

In the CL spectroscopic method the important parameters that required optimisation include:

- Polymer ageing temperature
- Length of the ageing period
- Degradation medium
- Scanning interval for the CL emission spectra
- Scanning wavelength for the CL spectra

The ageing temperature was selected after initial low temperature ageing experiments. At low temperature i.e. upto 150ºC, the CL signal was faint, and required very long ageing to detect any significant variations in the degradation behaviour of the polymer. Further, in solid-state the CL signal from a polymer is exposed to interference from the compositional and structural heterogeneity of the sample. Selection of 200°C as the degradation temperature for CL analysis was made due to its proximity with the processing conditions for the polymer. The temperature is also reported generating optimum CL emission in PP. The experimental/degradation period for each sample analysed here was different and characteristic of the composition of the sample. A sample was scanned for emissions from the inception of sample heating until the time the CL signal reached a maximum value. Sample degradation for CL emission was done in presence of air. It not only made it closer to the experimental conditions used in the IR and emissions analysis but also to the real life conditions exposed to a polymer during processing and service life.

The scanning wavelength for CL emissions spectra was done for 300-700 cm^{-1}, the wavelength range generally defined as forming CL emissions from polymers. The signal amplification for CL emission spectra required the emission to be acquired every 10 min. The 10 min interval was selected after initial scanning for shorter intervals.

3.3. Chromatographic and mass-spectrometric methods

Low molecular weight degradation products of volatile and semi-volatile nature evolved during thermo-oxidative degradation of PP formulations were analysed by gas chromatographs in connected with flame ionization or mass spectrometric detectors. Prior to the chromatographic

analysis, emissions from the samples were trapped using various trapping/extraction/enrichment methods reported in literature for the analysis of volatiles. Static headspace (SHE), thermal desorption (TD), solid-phase micro-extraction (SPME) and micro-scale sealed-vessel extraction (MSSV) were compared, before finally selecting SPME and MSSV for the final analytical work. The key elements of method development for the GC, MS, and the extraction methods are discussed in the rest of the current section. Before a detailed discussion however, there are few points that need attention:

- The GC analysis, except for the thermal desorption method (conducted using a GC-FID), was done using an MS detector.
- Irrespective the type of pre-analytical extraction technique, the key parameters for the GC (3.3.3) and the MS (3.3.4) method were the same throughout the work.
- Any changes in the basic GC-MS method, inevitable due to procedural requirement of the extraction techniques, e.g. low inlet temperature in MSSV-GC-MS method, are reported in the corresponding methods (Section: 2.3.3.1a-2.3.3.1d).

3.3.1. Gas Chromatographic method

A reliable identification and quantitation of the components of a mixture by GC requires the mixture to be eluted with sharp and well-separated peaks within a reasonably short elution period. These conditions are generally met through appropriate selection of a GC column, mode of sample injection, and an optimum oven temperature programme.

Selection of a GC column is typically dictated by four important factors: a stationary phase, internal diameter (i.d.), stationary phase film thickness, and length of the column. The stationary phase is generally selected on the basis of the principle ‘like-dissolves like’; a column with a non-polar stationary phase is therefore, generally used for a non-polar mixture while a polar phase for a polar mixture. Although PP has been reported to produce both polar and non-polar compounds, the latter group tends to pre-dominate. A non-polar capillary column, with a slight polar character was selected right from the beginning. The selection of a partly polar column was also supported by contemporary literature [15, 50, 102, 103, 108, 112, 115]. The capillary columns are commercially available with a range of internal diameters (i.ds) i.e. 0.10-0.53 nm. A column with an i.d < 0.25 nm provides a better peak separation in less time but is prone to fast saturation at high concentrations. Columns with smaller i.d. are also not recommended for headspace GC analysis by the manufacturers. Increase in the i.d. makes a column better at

accommodating higher concentration but at the cost of peak separation and elution time. Selection of an appropriate i.d. therefore, means a compromise between the optimum peak separation and analysis time. A 0.25 nm column has been used in most of the analytical separation experiments for the emissions from polyolefin. It is commonly used for the samples that are neither too low nor too high in their concentration, and has a separation capacity for a mixture of 50-100 compounds. After the i.d. was finalised, two columns with the length of 30 m and 50 m were tested before finally selecting the former on the account of short elution time [79, 116, 117].

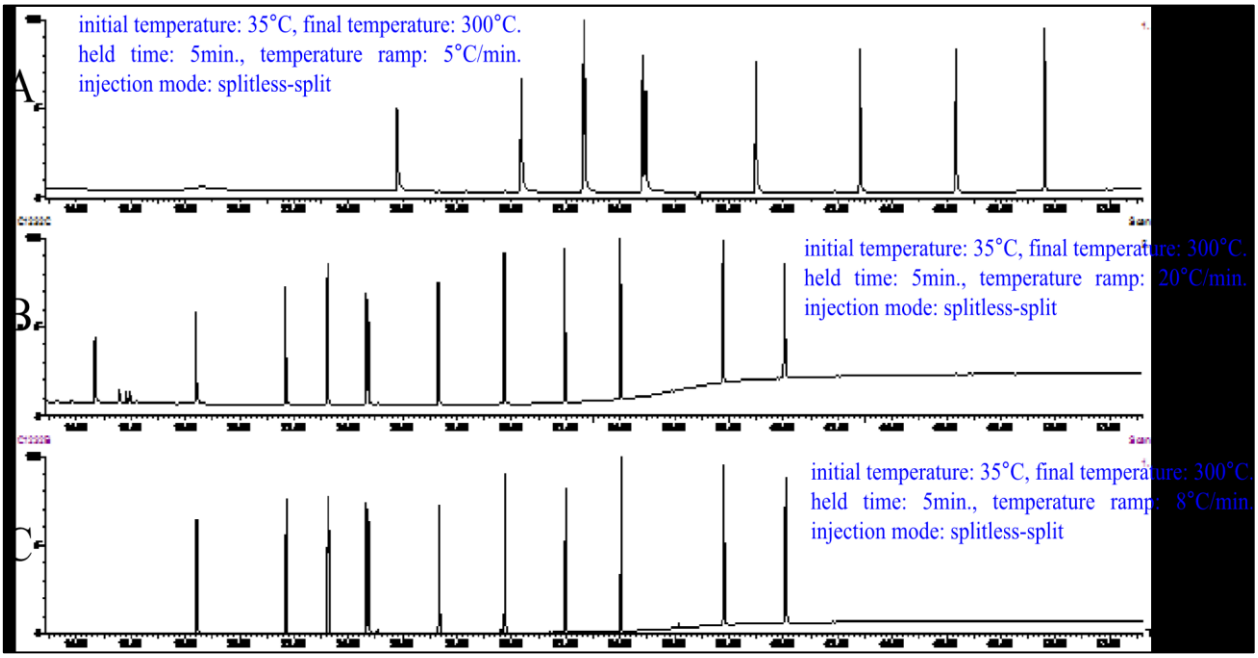


Figure: 3.5. A comparison of the GC-oven programmes.

GC is based on the principle of sample volatilisation and its subsequent separation through the column. Volatilisation can either be obtained isothermally or through a gradient temperature programme. In the former, the temperature of a column/GC oven is increased to one particular level and kept the same during the course of analysis. The isothermal separation allows an instant separation of the components of a mixture, hence taking less time. It is generally useful for a mixture of compounds with narrow boiling window. In the gradient temperature programme, the column temperature is ramped at regular intervals allowing the separation of a mixture of compounds with a broad spectrum of boiling points. Additionally, a gradient programme offers higher sensitivity and allows better peak shape even at higher molecular weight range. Since the PP emissions are expected to be a varied mixture of compounds, a gradient oven programme was preferred for the current work.

Three different gradient temperature programmes have been tested before selecting a final programme that covered the same temperature range but varied in the ramp rate (Figure: 3.4). Among the three different ramp rates: 20 ºC min^{-1} lead to incomplete separation of some peaks among the low boilers (Figure: 3.5B), while 5 ºC min^{-1} resulted in wide spacing, and hence long elution period. A better compromise between separation window and analysis time, 8 °C min^{-1} (Figure: 3.5C) was selected as the optimum ramp rate for the oven programme [118].

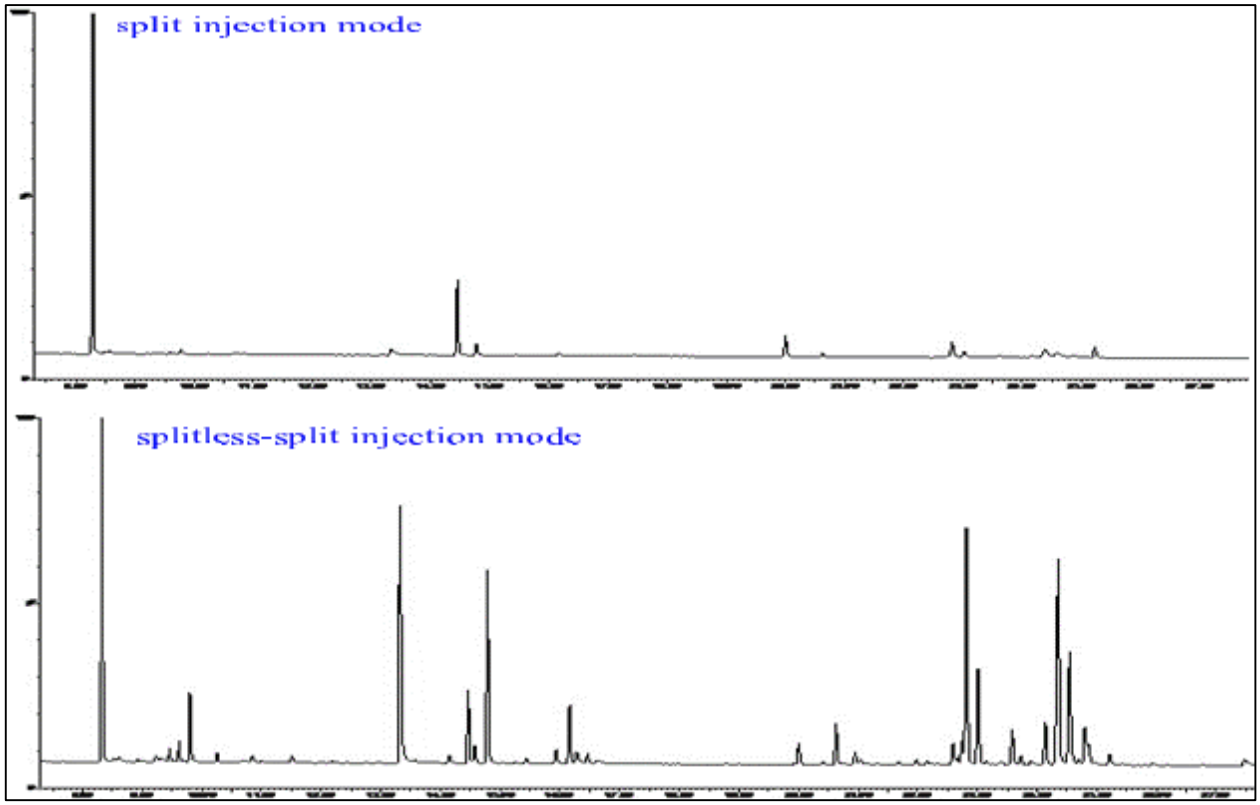


Figure: 3.6. A comparison of the GC sample injection modes.

GC sample injection modes were tested for method optimisation. Both the splitless/split and split modes were tested for the current work revealing the former as the more appropriate strategy to be followed for the rest of the work (Figure: 3.6.). A splitless/split mode allows uninterrupted introduction of the sample for a pre-determined period followed by splitting into column stream and disposal stream [118, 119]. The splitless/split mode is preferred for low concentration levels where it can increase the sensitivity of the method, and is avoided for high concentration samples to undermine the risk of column clogging; column saturation or peak tailing could be avoided. One of the advantages of solvent-free extraction methods is that the sample is free of a solvent and has significantly lower level of contaminants, a splitless/split injection therefore, was less risky for the current work.

As shown in the Figure: 3.6, a significant increase was observed in the sensitivity of the overall method when the split injection was replaced by splitless/split injection. The splitless/split injection not only resulted in an increase in the intensity of the total ion chromatogram, but also showed greater number of peaks. Hence, many compounds that were wasted into purge stream in a split injection were successfully loaded onto the column in the splitless/split injection.

A chromatographic system has numerous sources of contamination: column, septum and inlet liner being the main ones. Further, the high sensitivity of a GC-MS system has the drawback of detecting any contaminants in the surrounding environment, in solvents, and in the experimental equipment etc. In addition to parameter optimisation, the sources of contamination needed to be carefully monitored and eliminated. In the current study, column bleeds were reduced by column conditioning, while the contaminants were ruled out by running column blanks before and between test runs. Method blanks were conducted to identify contaminants from experimental procedure. Before a test run, a peak free chromatogram, as shown in the Figure: 3.7, was generated. The non-zero base line in the blank is due to siloxanes, which increases at high boiling range, and is typical of GC. Since the chromatographic calculations are relative, as long as there is no ghost peaks and the siloxanes masking or co-elute with a target peak, a non-zero base line of the chromatogram does not affect data.

Prolonged use of a GC column and occasional leaks in a GC system as well as use of reactive analytes can affect the quality of a GC column and hence its performance. A reliable data needs careful monitoring of the condition of the stationary phase on the column. In the current study, the instrumentation calibration was done using a hydrocarbon mixture of the range C12-C32. A well sustained peak intensity throughout the chromatogram, sharp peak shape, and separation was used as the criterion to assess the working condition of the column and the over-all GC instrument . Any damage in the column or formation of active sites along the pathway (syringe, inlet etc.) of the mobile phase leads to decrease in the intensity of the peaks (especially in the higher boiling region), greater column bleed, and peak broadening. For the current work, sharp peak shapes and a sustained sensitivity was made sure even at high boiling region of the corresponding chromatograms (Figure: 3.8).

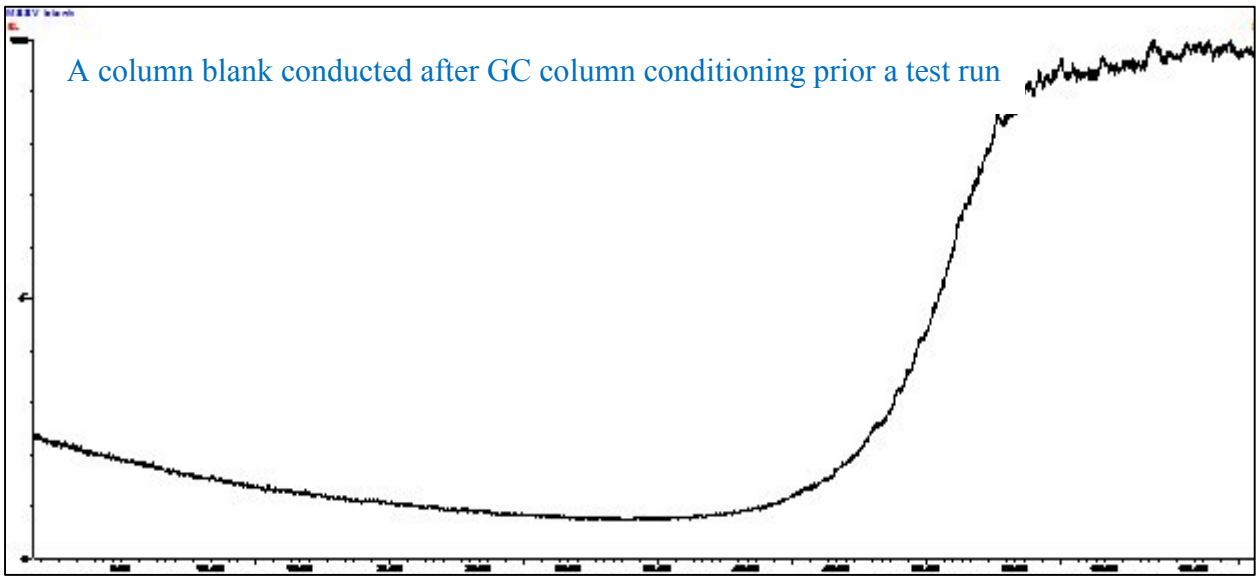


Figure: 3.7. A chromatogram of the GC Column-blank.

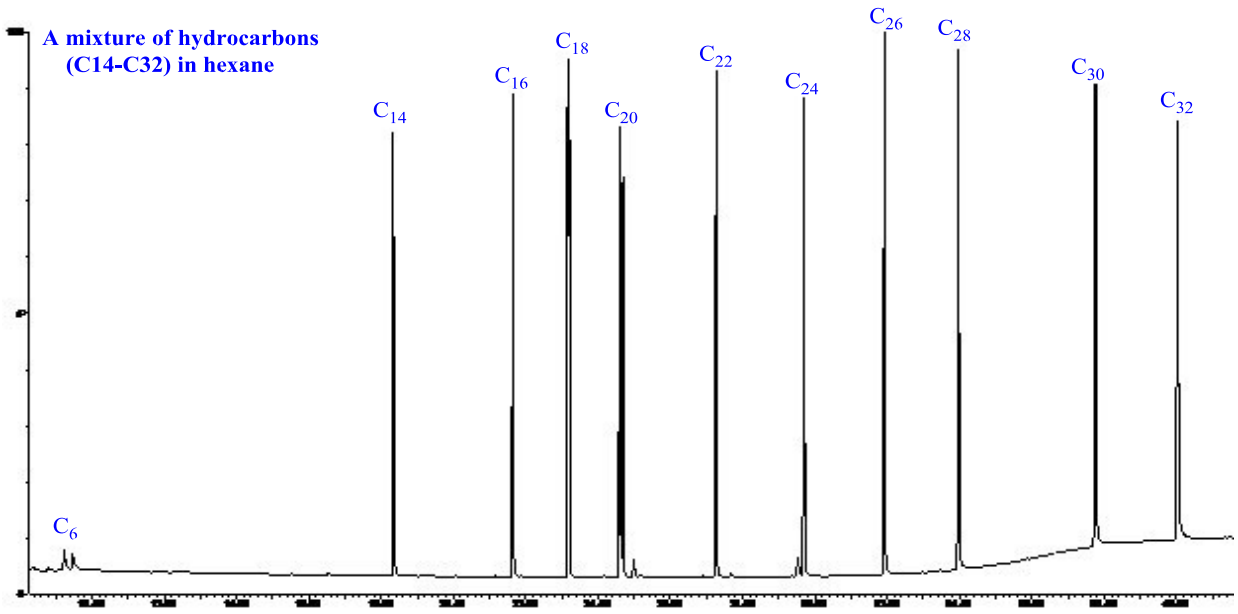


Figure: 3.8. GC-system optimization using a hydrocarbon mixture in hexane.

Peak tailing, one of the commonly encountered problems in GC based analysis, was detected initially. As far as the reasons of peak tailing are concerned, it is a broad area and varies with the chemistry of a sample, type of column, and the sampling technique used. Peak tailing can affect reliability in identification and quantitation of peaks by masking small peaks, and reducing their slop, respectively; the automated peak integration algorithms take the shoulders into account making it an important source of error.

For the current work the peak tailing was deduced to be due to the sample being injected in a comparatively narrow band and was typical of a capillary column. This problem is typical of

SFE methods of injection, which allow sample injection and hence subsequent column loading, over extended period. The problem was sufficiently resolved using cryogenic focusing. It was observed that immersing a small section of the injection end of the column in liquid nitrogen for initial five minutes made the peaks more symmetrical in shape (Figure: 3.9). Through this so-called cryo-focusing, the sample was allowed to desorbed and get accumulated at a short column loop before exposing to separation through the column length.

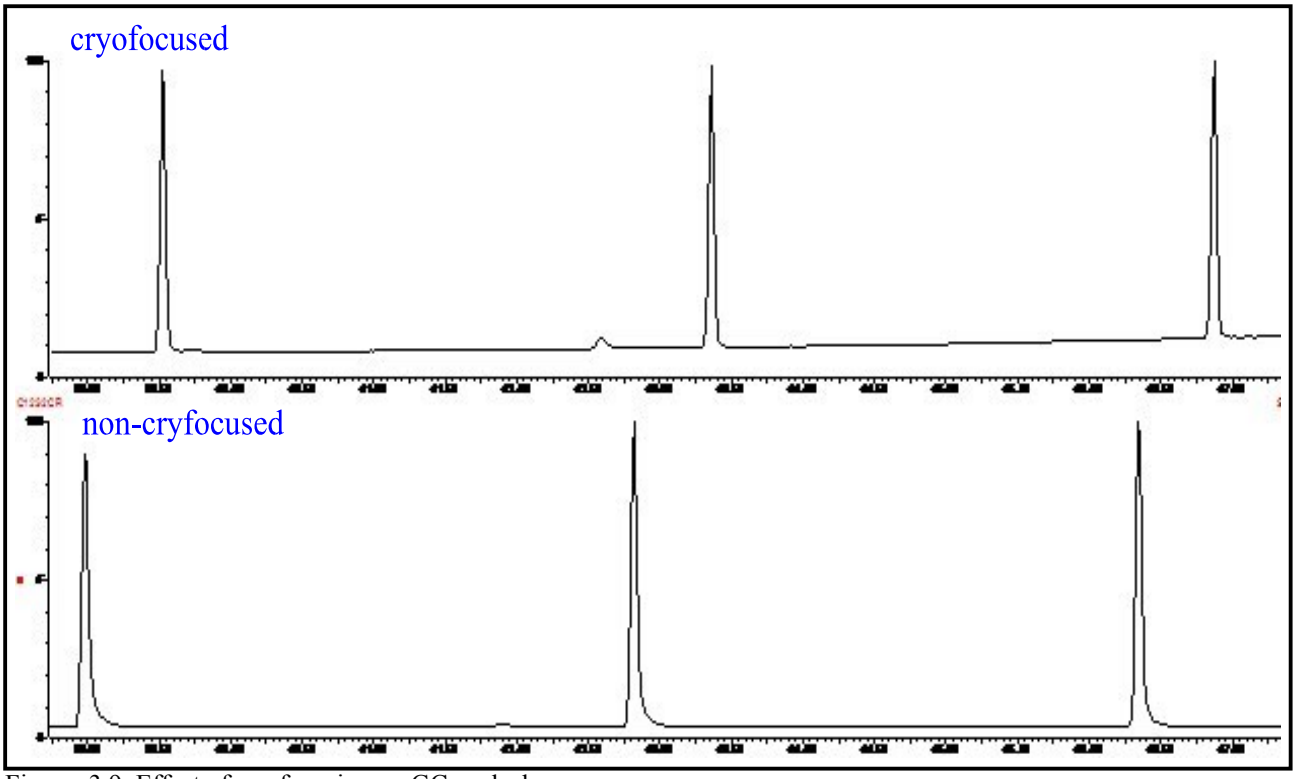


Figure: 3.9. Effect of cry-focusing on GC peak shape.

3.3.2. Mass Spectrometric Method

A quadruple mass spectrometer that was used for the current study, is commonly used either in selective ion monitoring (SIM) or a full scan mode. The former is typically preferred for the sample of known chemical nature as it allows better resolution in less time while the latter is typically used for the sample of unknown nature. The full scan method allows a scan of an m/z range with an upper limit of 1000, detecting a multitude of compounds falling in the range [120]. The m/z range selected for the current study was 35-500 Th. The range was selected as it covers most of the volatile and semi-volatile compounds in nature and synthetic sciences. Although the lower end of the range i.e. 35, could be reduced further to identify some more important volatiles, it avoided due to the chances of potential noise generated by gases in the air, e.g. nitrogen at 28 and oxygen at 32 etc. The higher end of the mass range i.e. 500 Th, was found

appropriate as the chromatogram seemed to level off long before 500 Th, for all samples tested during method optimisation.

At the start of a working day and later as and when required, the mass spectrometer was manually tuned for the m/z: 69, 212 and 502 of perfluoro-tetradecanoic acid (PFTA). Any leaks in the GC-MS system were continuously monitored throughout the experimental work, by comparing the peaks for water and nitrogen. In a leak free system, nitrogen peak in the MS is expected to have an intensity greater than that of the water vapours. Both peaks tend to subside over time as the vacuum builds inside the MS.

Unlike conventional GC methods, where an unknown can only be identified by comparing it with a reference compound, GC-MS has an advantage of identifying the compounds on the basis of their molecular weights. In the current study, molecular ion peaks identifiable (where detected), fragmentation patterns, base peaks, and the relative position of the peaks in a TIC was used to identify the large number of unknown compounds detected during the current study (Section: 3.3.1). MS databases i.e. NIST and Wiley libraries of mass spectrometry, along with the references from relevant published literature provided help in better identification of the unknown compounds (Figure: 3.17-3.25 and Section: 3.3.4).

Quantification was conducted through automated peak integration on Mass Lynx (3.26). The peak areas are reported in percent relative terms throughout the work (Chapter: 6). This approach provides a convenient way to compare the emissions for the formulations.

3.3.3. Volatile extraction methods

The four different extraction methods: HSE, TDA, SPME, and MSSV, tested for their suitability for the current study were found to vary significantly in the range and total yield of the volatile that could extract from the sample (Table: 3.1).

Table: 3.1. The list of the volatiles extracted from the sample B using four different extraction methods. (dSPME; dynamic solid-phase micro-extraction, SHE; static headspace extraction, TD; thermal desorption, MSSV; micro-scale sealed-vessel, sSPME; static solid-phase micro-extraction).

m/z	Sampling techniques	dSPME	SHE	TD	MSSV	sSPME
44	Carbon dioxide	*	*	*	*	
48	Sulphur monoxide	*				
42	1-Propene	*			*	
50	1,3-Butadiyne				*	
58	Acetone				*	
60	Acetic acid				*	
96	2,4-dimethyl-1,4-pentadiene					
50	1-Propyne				*	
44	Acetaldehyde		*			
59	2-Propaneamine				*	
68	1,4-pentadiene					
56	1-Propene, 2-Methyl	*	*		*	
72	Pentane		*			
58	Butane	*			*	
62	unknown					
76	Propane, thiol	*				
86	Pentane,2-Methyl	*	*		*	
84	Cyclopentane, Methyl				*	
78	Benzene	*			*	
70	Methacrolein	*				
86	Hexane	*	*		*	
84	Cyclohexane		*			
70	2,5-Dihydrofurane	*			*	
84	3-Methyl-2-Pentene	*				
94	Dimethylsulfone					
86	Pentane,3-Methyl	*	*			
72	Propanal,2-Methyl	*			*	
60	Acetic acid	*				
84	2-Methyl-1-Pentene	*				
84	Cyclopentane, Methyl				*	
84	Cyclobutanone,2-Methyl					
84	2-Hexene				*	
100	Hexane,3-Methyl	*	*			
96	2,4-Dimethylfuran	*				
98	4-Pentene-2-one	*				
100	Heptane	*				
114	Heptane,4-Methyl				*	

128	Heptane, 2,4-Dimethyl				*	
114	Octane	*				
92	Toluene	*	*		*	
100	2,4-Pentanedione	*				
96	2,4-Dimethylfurane	*				
114	Pentane, 3-Ethyl		*			
126	2,4-Dimethyl-1-Heptene	*				
98	2-Pentene,4,4-Dimethyl				*	
128	Octane, 4-Methyl	*	*		*	
128	2,3,4-Trimethyl, Hexane	*				
128	Heptane,2,4-Dimethyl				*	
98	4,5-Dihydro-2,4-Dimethyl				*	
100	Heptane					
106	Xylene	*	*		*	
126	Isopropylhtdrazone,2-butenylaldehyde	*				
126	Octane,6-Ethyl-2-Methyl				*	
126	6-ethyl-1-Octene				*	
128	Hexane 2,3,5-Trimethyl	*			*	
138	4-Acetyl-1,3-Dimethylpyrazole	*				
140	3-Octen-2-one,7-Methyl	*				
154	Ketone,2,2-Dimethylcyclohexyl Methyl	*				
120	Benzene,1,3,5-Trimethyl	*			*	
142	2,4-dimethyl-4-pentenoic acid methyl ester	*				
168	1-Dodecene				*	
136	limonene	*				
170	Dodecane	*			*	
338	Tetracosane				*	
226	Hexadecane				*	
138	1-Methyl-4-1(1-methylethyl)cyclohexene	*				
140	3,3,5-Trimethylcyclohexanol	*				
128	3-Isopropyl-6-Oxoheptanoic acid	*				
140	1-methyl-4-(1-methylethyl)-cyclohexane	*				
122	Benzoic acid	*				
140	2-Dimethylamino-4,5-Dimethyloxazole	*				
210	Pentadecene				*	
212	Pentadecane	*			*	
210	5,5-Dimethyl-1,3-hexadiene				*	
160	unknown	*				
172	Benzene,4-Heptynyl					
149	Phthalate				*	
240	Heptadecane					
232	6-Hydroxy-5-Methoxyangelicin				*	

234	unknown					
236	1,1,3-Trimethyl-3-Phenylindan	*				
234	2,6-Di-Tert-Butyl-4-Ethylphenol				*	
252	Octadecene				*	
254	Octadecane	*			*	
248	2,5-Di-tert-Amylquinone	*			*	
248	2,6-Di-Tert-Butyl-4-Isopropyl Phenol				*	
220	Phenol,4,6-Di(1,1-Dimethylethyl)	*				
220	BHT				*	
124	3,5-Dimethylcyclohexene-1-one	*				
140	Heptadecane	*				
206	Phenol 2,4-Bis (1,1-Dimethylethyl)	*			*	
202	1,4-Methanobenzocyclodecene, decahydrate	*				
210	Naphtho 1,2-B Furan,2,3-Dihydro-2-(Methyethyenyl)	*				
296	Heneicosane				*	
338	Tetracosane				*	
380	Heptacosane				*	

3.3.3a. Static headspace (SHE)

SHE was initially selected as an extraction technique mainly on the account of its fast, simple and convenient execution nature. Method development for SHE included optimising the modes of injection, vial and transfer-loop pressure, and headspace equilibration and transfer time (Section: 2.2.2b). After a series of experiments that were conducted over a range of ageing time and temperature for PP formulations, it was found that the technique was unable to detect any thermal and temporal changes in the emissions as the polymer aged. Further, the emissions made by the formulations stabilised with different antioxidant packages did not show any marked differences (Table: 3.2). The emissions detected by this method were merely hydrocarbons.

Unlike the range of degradation products that have been reported in literature on degradation of PP [68, 103, 115], all that could be detected with SHE-GC-MS during the current work consisted of: hydrocarbons with a chain length of C3-C9, benzene, toluene and carbon dioxide. No stabilised-based degradation products were detected in emissions from any of the formulations. The technique therefore, was considered to have an inadequate sensitivity for the level of emissions made by stabilised PP formulations. The Applications of this method in literature have been observed to be restricted to emissions from the un-stabilised PP. Presence of stabilisers reduced PP degradation making the emissions below the detection limit of SHE.

Table: 3.2. PP emissions measured using SHS method.

		Sample i.d.		
m/z		B	O	G
	Name of degradation product	Retention time (Rt)		
44	Carbon dioxide	1.66	1.66	1.66
56	2-Methyl, propene	1.22	1.22	
72	Pentane		1.37	
86	Hexane	1.74	1.75	1.75
86	2-Methyl, pentane	1.59	1.59	1.59
86	3-Methyl, pentane			1.66
84	Cyclohexane	2.25		2.25
84	Methyl, cyclopentane		1.95	1.95
98	Methyl, cyclohexane	3.02		
128	Nonane	6.2	5.08	5.09
92	Toluene		3.83	3.83
106	Xylene		6.32	
142	3-Ethyl, 3-methyl, heptane	12		

3.3.3b. Thermal desorption (TD)

In the TD-GC-FID analysis five different PP formulations i.e. A-D and O in the Table: 2.3, were analysed according to the VDA-278 protocol. This method is a standard protocol designed by 'vehicle development authority' for the analysis of emissions from non-metallic parts of vehicles. This method was adopted due to its importance as a standard method and also as a method against which any further methods could be compared later. Emissions from PP in this method were measured at 90°C and 120°C and reported as total emissions i.e. the sum of peak area corresponding to volatile and semi-volatile compounds. The highest level of emissions was observed for the formulation D (Table: 2.3) and can be attributed to low synergy between DSTDP and SN1010. As confirmed by the SPME and MSSV based results later in the study, the unexpectedly high emissions for the formulation were also due to the antioxidant degradation/emissions as well as the polymer. Although, under the same set of experimental conditions, the five formulations i.e. the formulations A-D and O (Table: 2.3 and 2.5), showed a significant difference in their total emissions (Figure: 6.2), the individual degradation products could not be identified by this method.

The qualitative dimension could be added to the data by replacing GC-FID with a GC-MS but at the cost of reproducibility. Unlike FID, a mass spectrometer utilises the ability of a compound to be volatilised ionised and fragmented. It is therefore not necessarily an accurate representation of its the absolute concentration in a mixture. Mass spectrometric results are therefore considered only semi-quantitative. Besides, access to a TD-GC-MS system was not possible at this stage. The cost of thermal desorption tubes and access to the related adsorption apparatus were the other factors that discouraged the continuous use of this technique beyond the initial sets of experiments. The results of TD experiments provided evidence that the emissions from the formulations stabilised with different additive packages varied significantly. The emissions at this stage were found to be mainly consisting of hydrocarbons.

Table: 3.3. Emissions from stabilised PP formulations measured by TD-GC-FID.

Total (volatile + semi-volatile organic compounds) emissions from PP formulations					
Sample i.d.	A	C	B	O	G
Total emissions	1.06 µg g^{-1}	16.62 µg g^{-1}	1.20 µg g^{-1}	<1 µg g^{-1}	1.49 µg g^{-1}

3.3.3c. Solid-phase micro-extraction (SPME)

The third technique that was used after the initial testing with SHE and TD, is SPME. SPME, although a comparatively new technique, has already found its applications in polymer analysis. The results obtained for the technique however, are controversial; in some studies it has been reported as a sensitive method capable of sufficient extracting capability for the degradation products of PP [50, 102, 121], in others it is shown not to be very useful technique [108]. The contradictory role of this technique can be due to variation in the extraction methods that significantly varied among the individual works. For example, when used in its static form with the headspace of a sample sealed and aged inside a vial for adsorption by an SPME fibre, the results were not very promising. The role of an SPME fibres coating is another important factor. Polyacrylic (PA) and polydimethylsiloxane (PDMS) based fibres, for example, exhibited poor adsorption capacity for the emissions from polyolefin. It is also important to add that the general condition of the adsorption coating, if not intact at the time of use, can produce unexpectedly poor results.

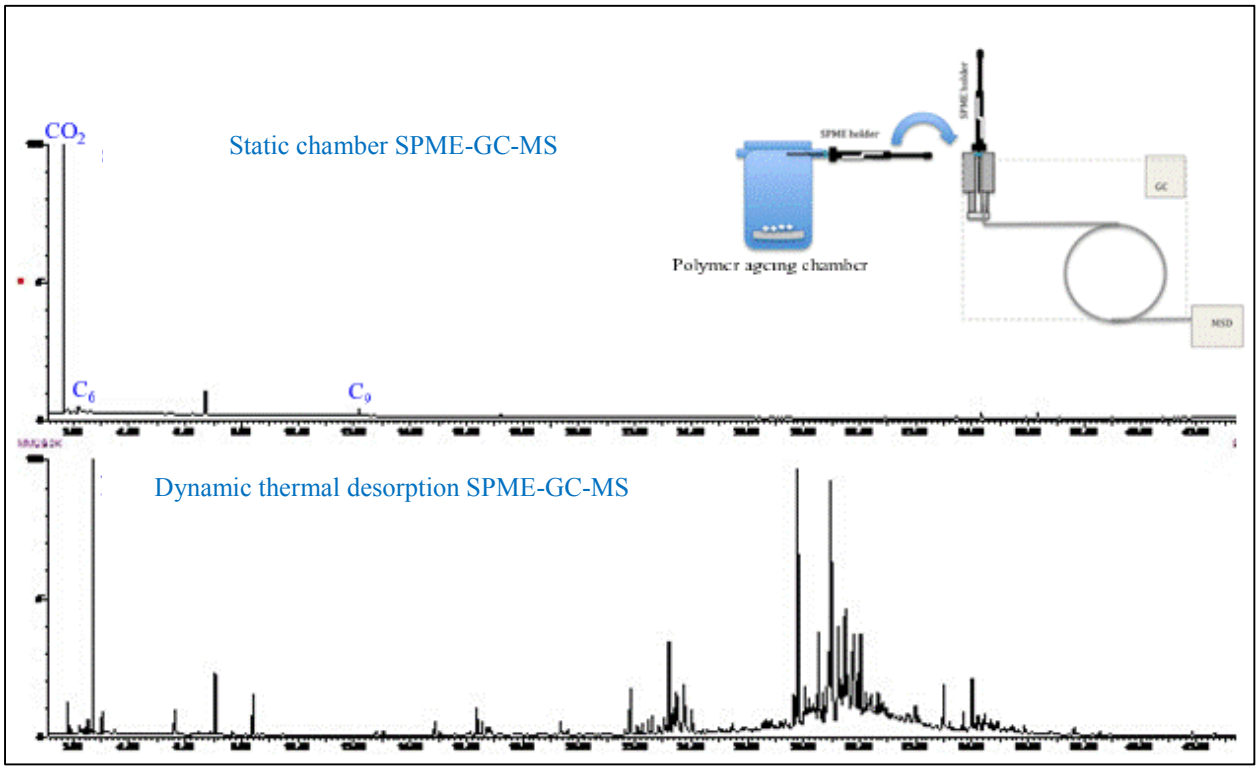


Figure: 3.10. A comparison of dynamic and static types of SPME-GC-MS methods.

In this context, it was imperative to carry out extended method development work for the SPME method. The key aspects that were optimised include ageing conditions, adsorption conditions, and the type of adsorption-phase on an SPME fibre . In order to compare the static and dynamic SPME approaches, initially a static SPME adsorption approach was used. It was conducted by allowing the SPME fibre exposed to a headspace over a polymer that was aged inside a sealed headspace vial. Over a range of temporal and thermal conditions, no significant variation on the emission could be detected. Assuming that the reason could be limited degradation due to only limited amount of air supply, the vial was replaced with an adsorption chamber, which was 20 times larger than a typical headspace vial however, no difference was observed in the results (Figure; 3.10). Finally, the static ageing and adsorption approach was replaced with a dynamic adsorption method. The dynamic adsorption was conducted on an adsorption unit that was assembled specifically for the current work (Figure: 2.6). The unit was capable of ageing the polymer under controlled conditions, e.g. temperature and airflow control, allowing a simultaneous ageing and adsorption of the emissions followed by their analysis on a GC-MS.

In order to find the most appropriate SPME adsorption phase, three fibres i.e. PDMS, CAR/PDMS and CAR/DVB/PDMS, were tested to compare their adsorption capacity. Under the

same set of experiment conditions, the fibres generated significantly different adoption profiles when tested for the same sample. As shown in the Figure: 3.11, it was found that the CAR/PDMS/DVB is capable of adsorbing polar as well as non-polar compounds, while the other two have a preference toward non-polar compounds. Further, the fibres also varied in the overall range of the compounds that could be adsorbed. The fibres were observed to show an adsorption order of CAR/PDMS/DVB > PDMS/DVB > PDMS for the total adsorption.

A range of experiments that were performed at various ageing temperatures and times showed that the technique is capable of detecting thermal and temporal changes in emissions profile (Figure: 3.12) as well as the stabilisation packages that were incorporated in the formulations (Figure: 3.13). It was possible to get a degradation profile as early as 10 min of ageing the polymer (Figure: 8.1 and 8.2.). As a convenient adjustment between the instrument availability and the trends in the variation in the emission profile, it was decided that emissions be measured after ageing time of 2 hrs, 8 hrs and 20 hrs. An SPME fibre is sensitive to all sorts of contaminations in the surrounding environment and inside the analytical system i.e. adsorption unit and the GC-MS machine. Besides, a poorly maintained and unconditioned fibre is also a source of siloxane-based bleeds that can interfere and affect the reliable quantification of an analyte.

This issue was addressed by conditioning the fibre, and running fibre and process blanks regularly throughout the experimental work. Conditioning was done by exposing the fibre to GC-inlet set at 300°C for a period of 30 min. The conditioned fibre was run at its own as a fibre blank (Figure: 3.13). A method blank was run by exposing the clean and conditioned fibre under experimental conditions. Generally, it was found to contain a carbon dioxide peak due to the presence of the gas in air that was run through the adsorption unit for ageing the polymer (Figure: 3.15).

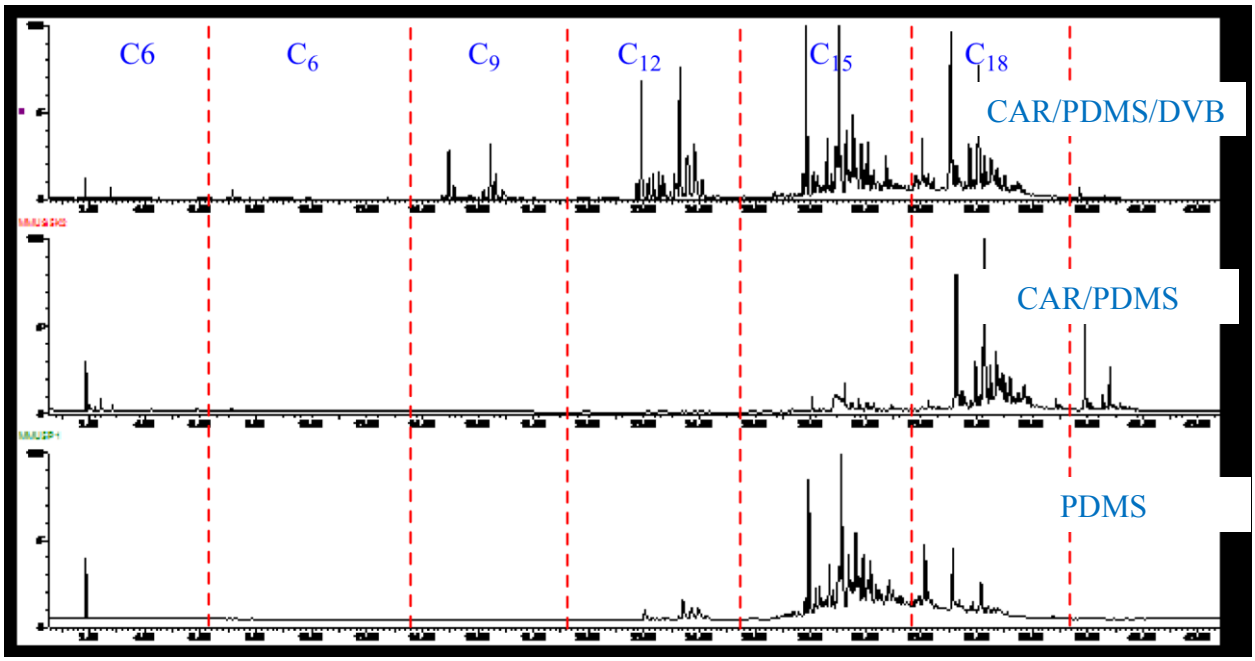


Figure: 3.11. A comparison of the absorption capacity of the three different SPME fibres.

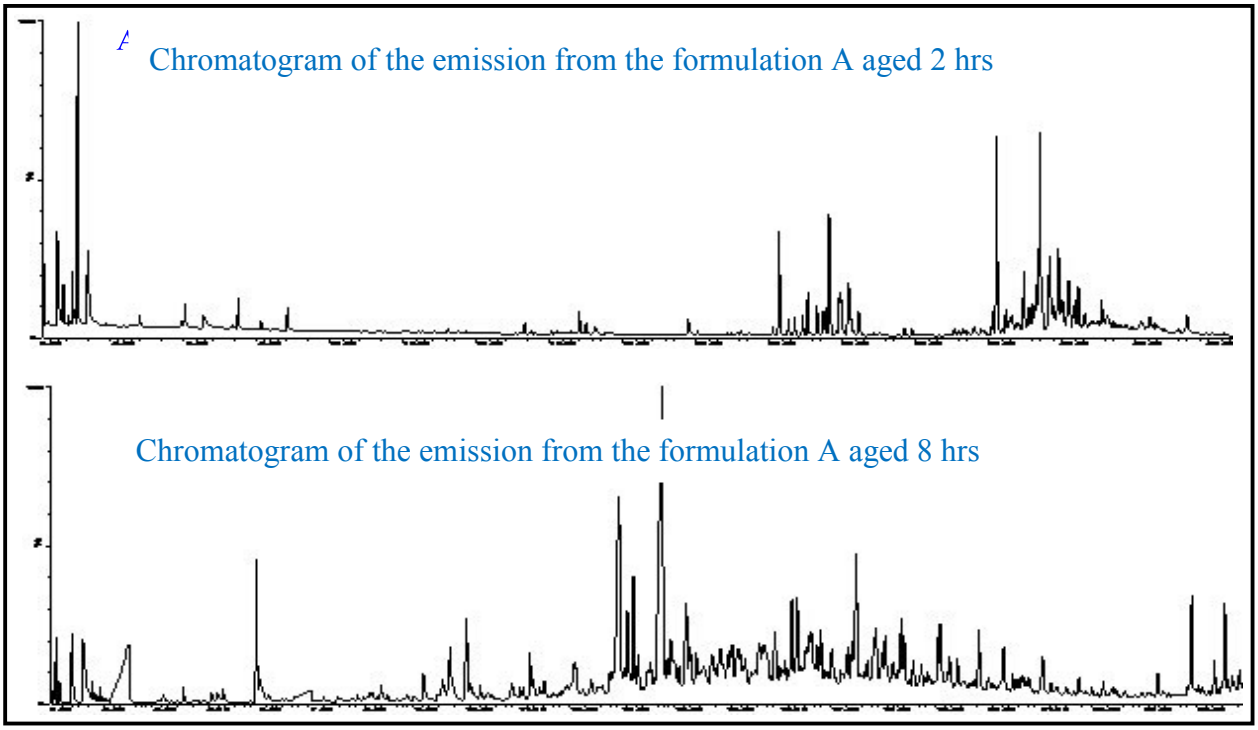


Figure: 3.12. Temporal variation in the emissions measured by dynamic SPME-GC-MS based method.

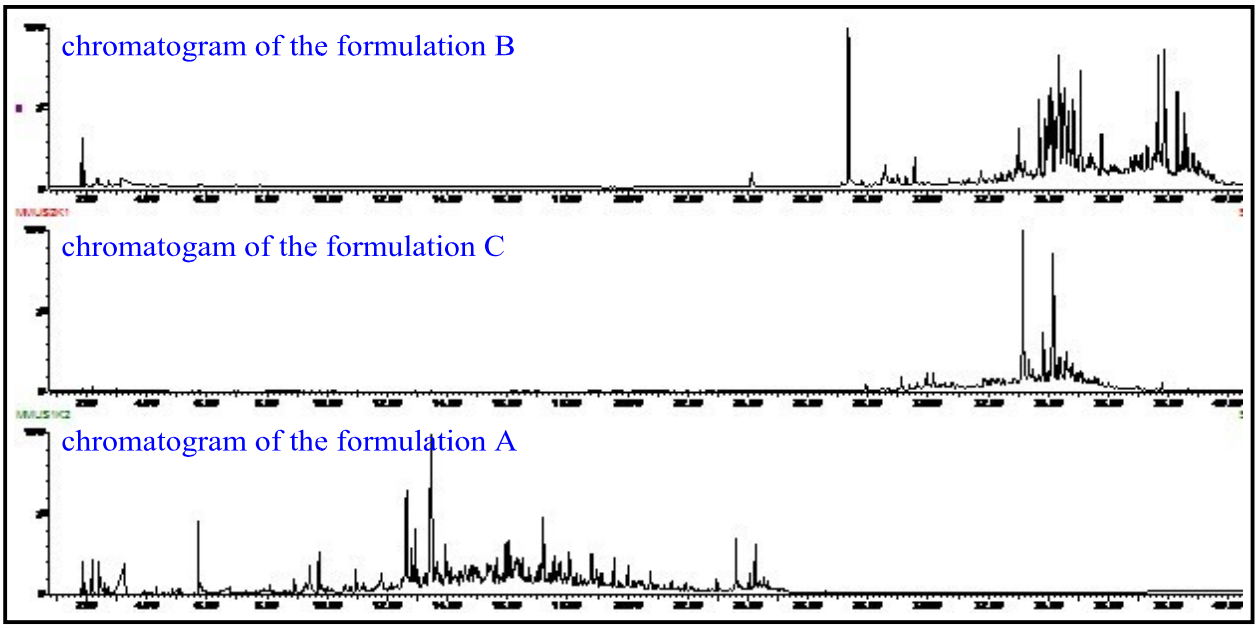


Figure: 3.13. Effect of stabilisation packages on the emissions from stabilised PP-formulations.

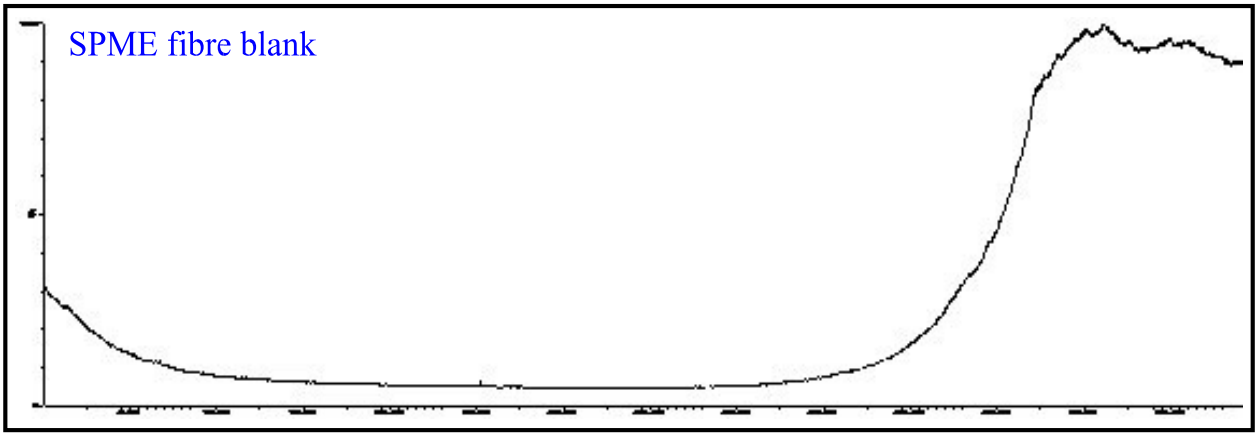


Figure: 3.14. A chromatogram of the SPME-fibre blank.

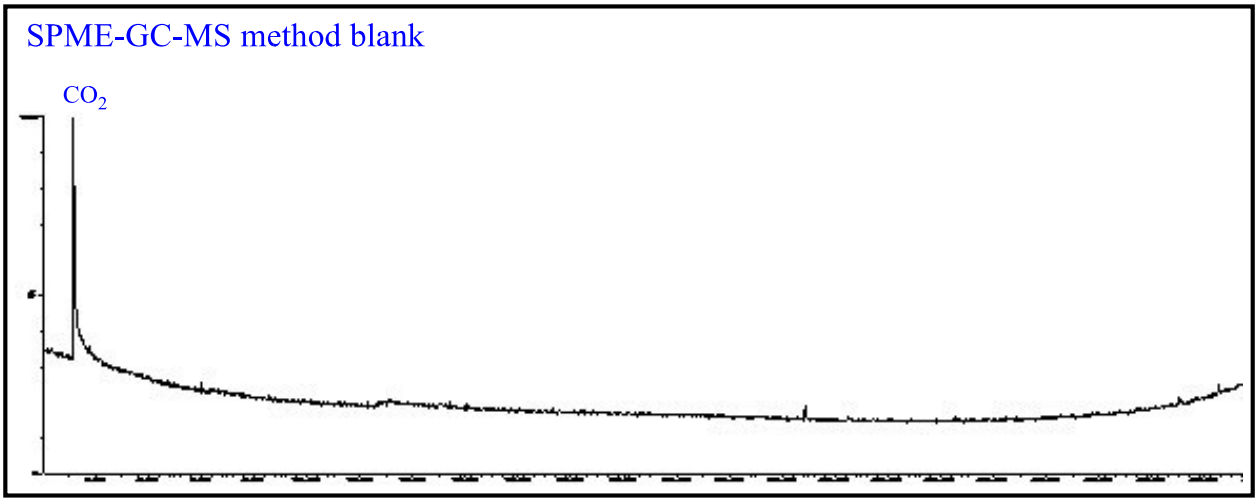


Figure: 3.15. A chromatogram of the SPME-GC-MS blank.

3.3.3d. Micro-scale sealed-vessel analysis

In order to investigate the limitations that could arise from selective adsorption of the SPME fibres used in the SPME-GC-MS method, MSSV-GC-MS was used as a complementary technique. Generally used for pyrolysis studies of geochemical samples, MSSV has rarely been used in polymer research. For the current work, the method was optimised for polymer analysis by reducing the polymer ageing conditions, and the temperature of the GC inlet liner, which was especially adapted for MSSV analysis (Figure: 2.7).

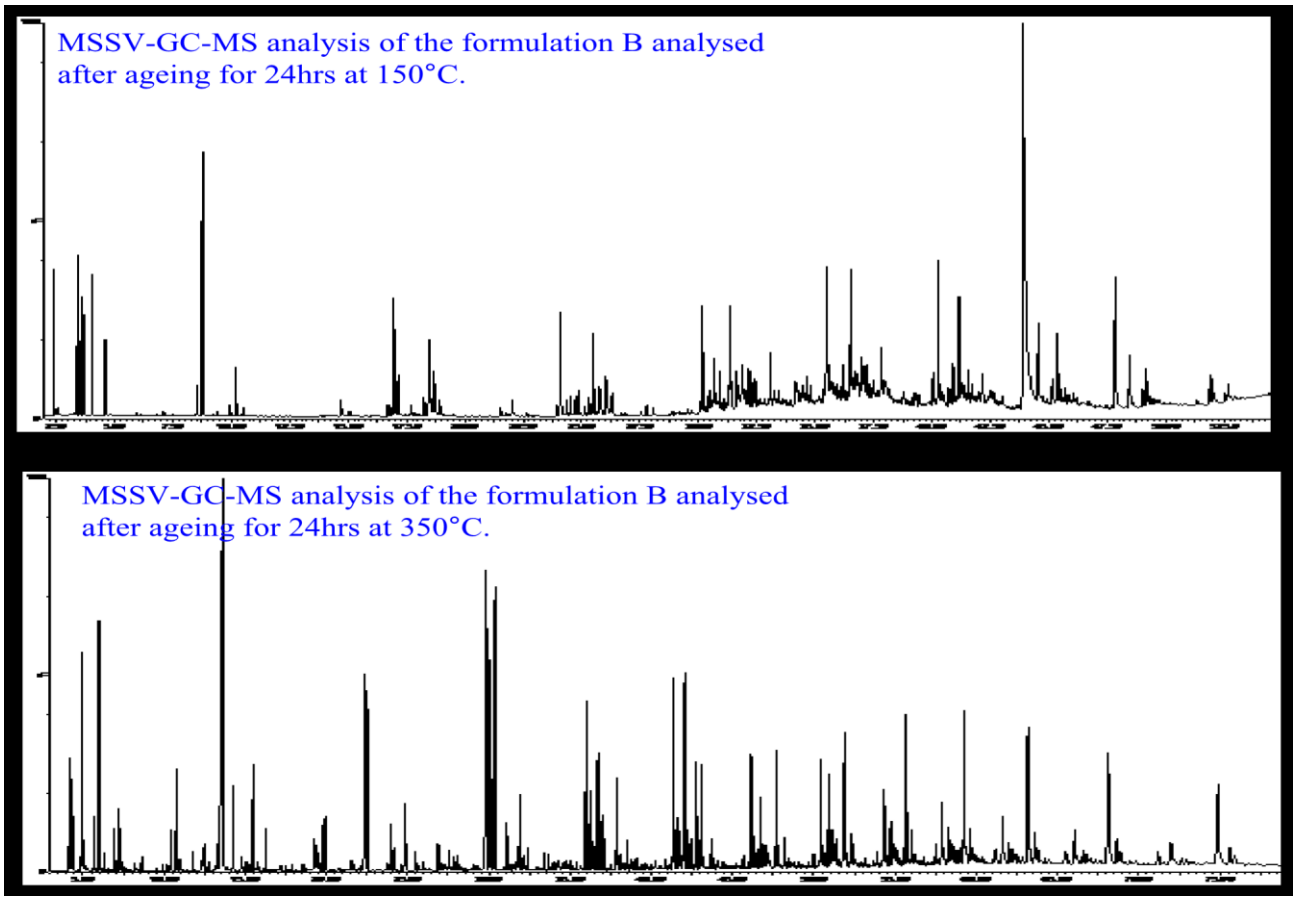


Figure: 3.16. Temperature optimisation for the MSSV-GC-MS method.

An MSSV liner was developed by replacing a conventional glass GC-liner with a metallic tube which was sealed at both ends and equipped with a retractable plunger. The possible sources of contamination in the MSSV experiments were removed by pre-cleaning the MSSV-tubes, filling and sealing them with the help of sterilised equipment. The GC-MS system blank run for MSSV were made on the empty liner, while a process blank was run on an MSSV tube that has been aged under the same experimental conditions as the rest, but with no polymeric sample inside. Although, in general, the MSSV results were comparable with those of SPME, the former contained more antioxidant-based fragment of polar nature (Table: 3.1 and Figure: 6.10-6.11).

3.3.4. GC-MS data Interpretation method

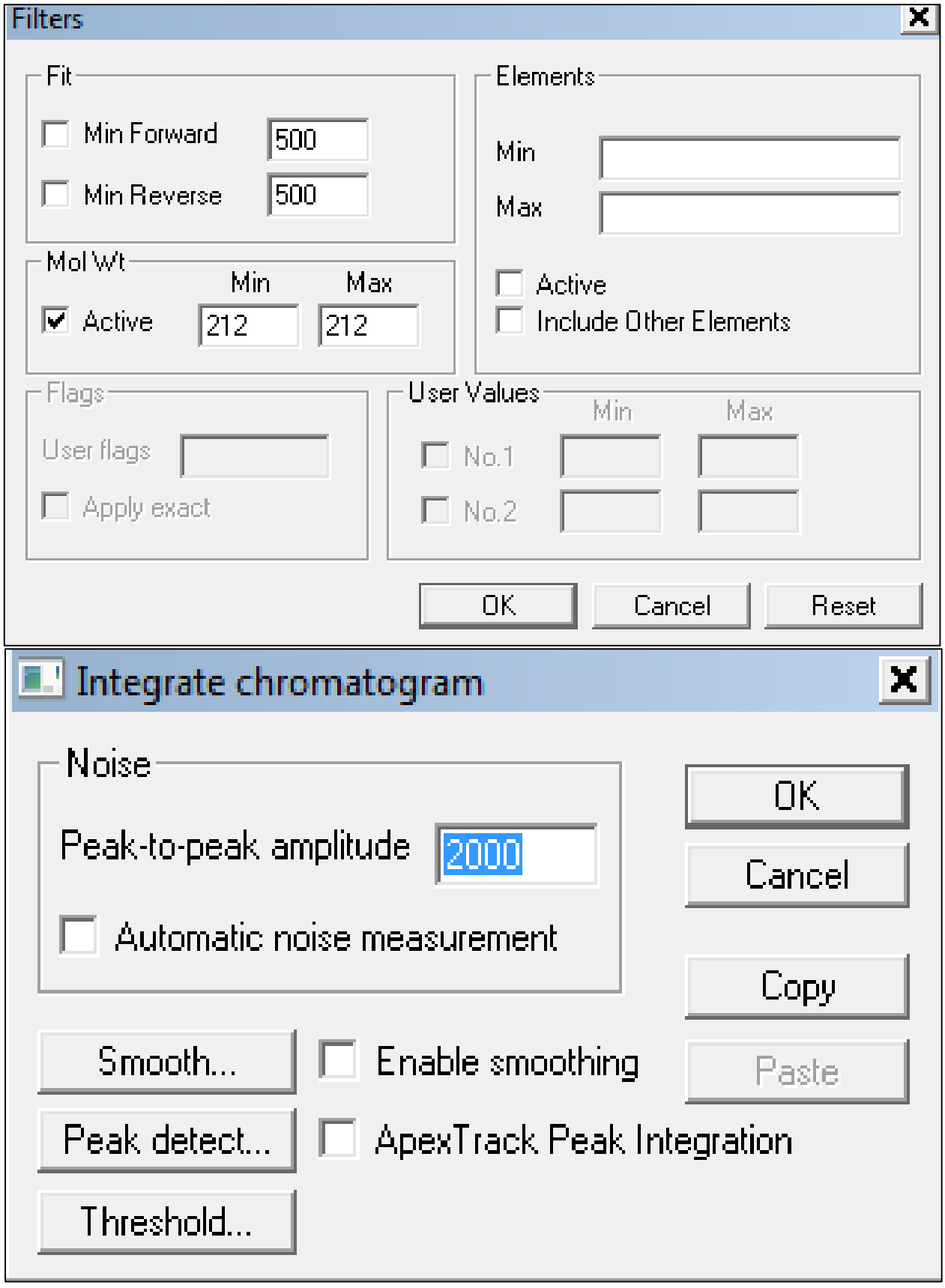


Figure: 3.17. Screen shots of the windows containing the parameters used in mass spectral library search (Filters) and chromatographic integration for quantification.

The GC-MS data once acquired as typical Total Ion Chromatograms (TICs), was processed for

- Identification of the peaks in a TIC followed by
- Quantitation of the identified compounds

The identification was done by comparing the mass spectra of the compounds with reference spectra in the NIST and Wiley libraries of mass spectral databases (Figure: 3.17-3.21). The countless possible spectral hits for each unknown were narrowed down by introducing mass filters in the library search. The mass filter was selected based on the given spectrum. In the spectra with a definite molecular ion, the m/z of the molecular ion was used as the mass filter. In cases where the molecular ion was not visible, a mass range within the limit of 35-500 was used as a filter. The general filter i.e. 35-500, could be narrowed down depending on the retention time of the compound as well as its mass spectrum.

While a significant number of the unknowns showed a good match with the library hits (Figure: 3.18-3.21), there were also compounds that had multiple hits. This problem was more common with hydrocarbons.

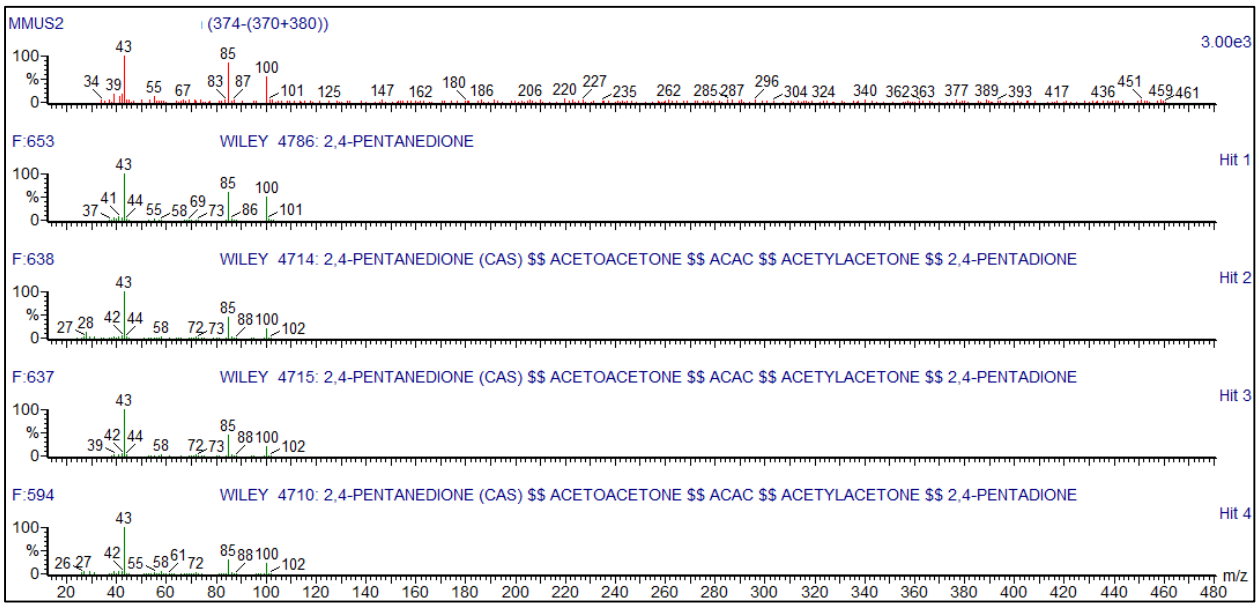


Figure: 3.18. A list of the mass spectral hits for an unknown peak, identified to be 2, 4-Pentanedione.

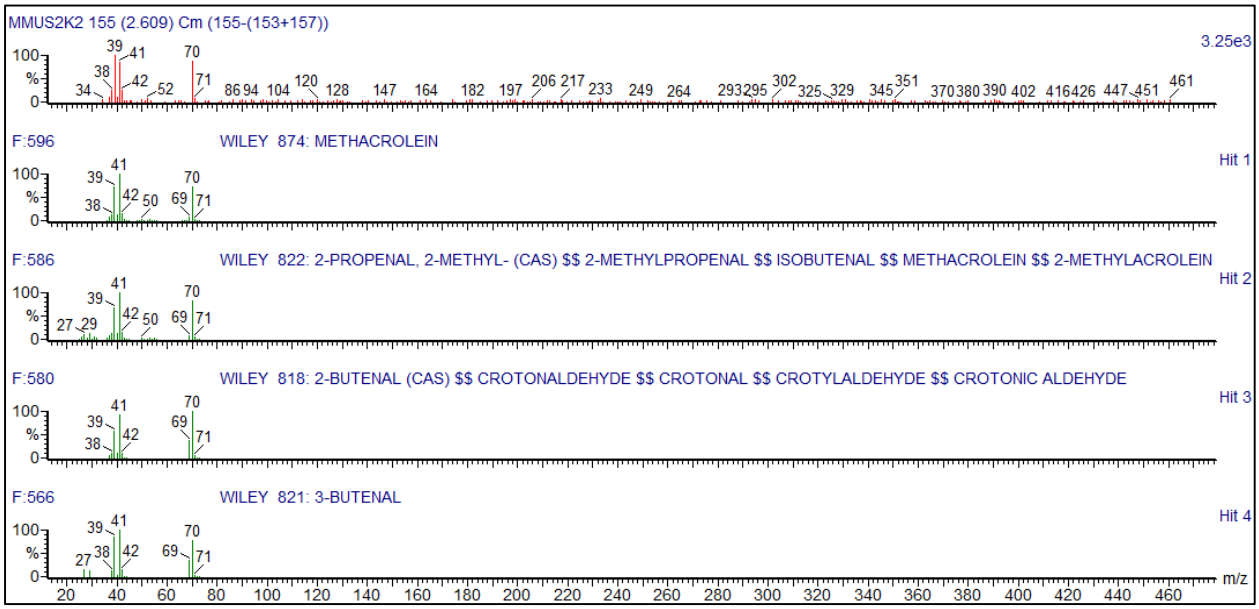


Figure: 3.19. A list of the mass spectral hits for an unknown peak, identified to be methacrolein.

The hydrocarbons generally showed multiple hits, mainly corresponding to various isomers of the same compounds. In such situation, the selection of the most likely hit was supported with the theoretical knowledge of the fragmentation pattern for the compounds. Increase in the molecular weight of the compounds, especially hydrocarbons, led to increase in the number of possible isomers, and hence difficulty in identification merely on the basis of library hits. The fragmentation patterns were therefore, a key part of the spectral assignments.

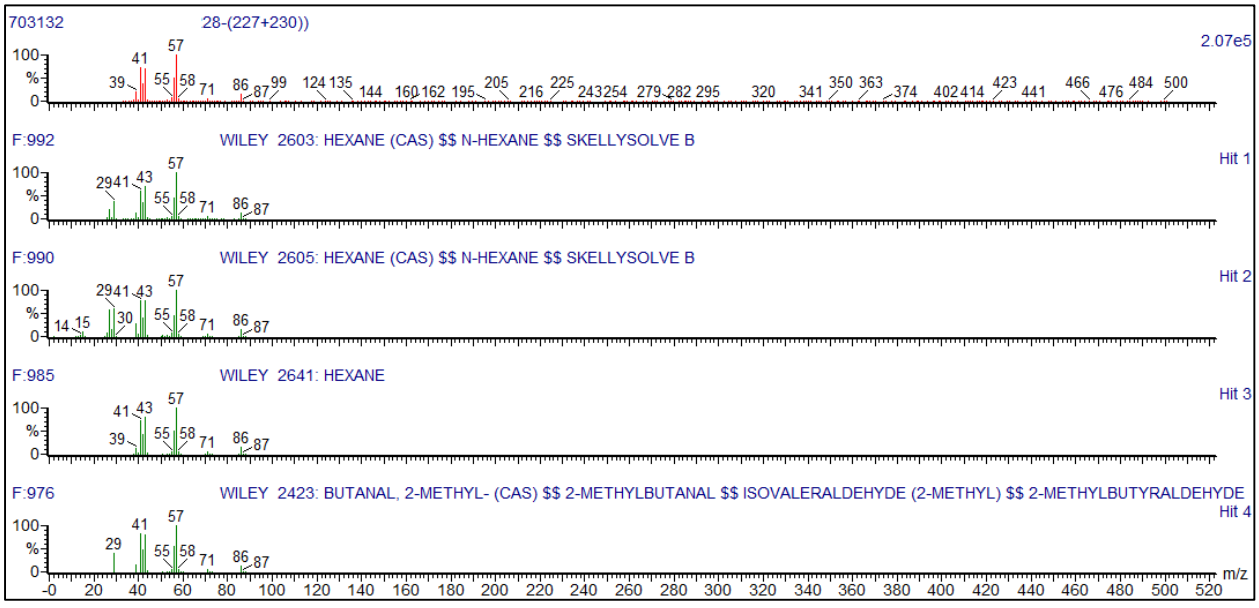


Figure: 3.20. A list of the mass spectral hits for an unknown peak, identified to be hexane.

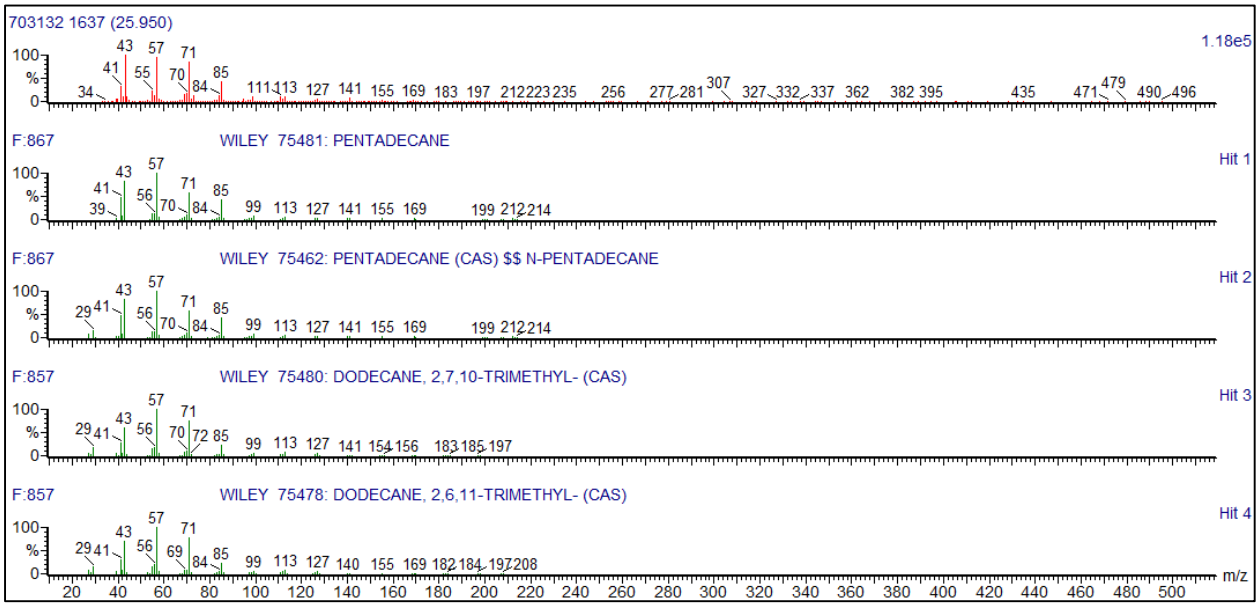


Figure: 3.21. A list of the mass spectral hits for an unknown peak, identified to be an isomer of pentadecane.

The fragmentation pattern identification was also very useful in the identification of carbonyls. carboxylic acid spectra, for example, were characterised by prominent peaks at m/z: 60, ketones had prominent m/z: 58 peak, while the aldehydes were identified by the presence of a peak at m/z: 82. The aromatics, similarly were characterised by prominent molecular ions as well as phenolic and benzene fragments in their mass spectra (Figure: 3.25).

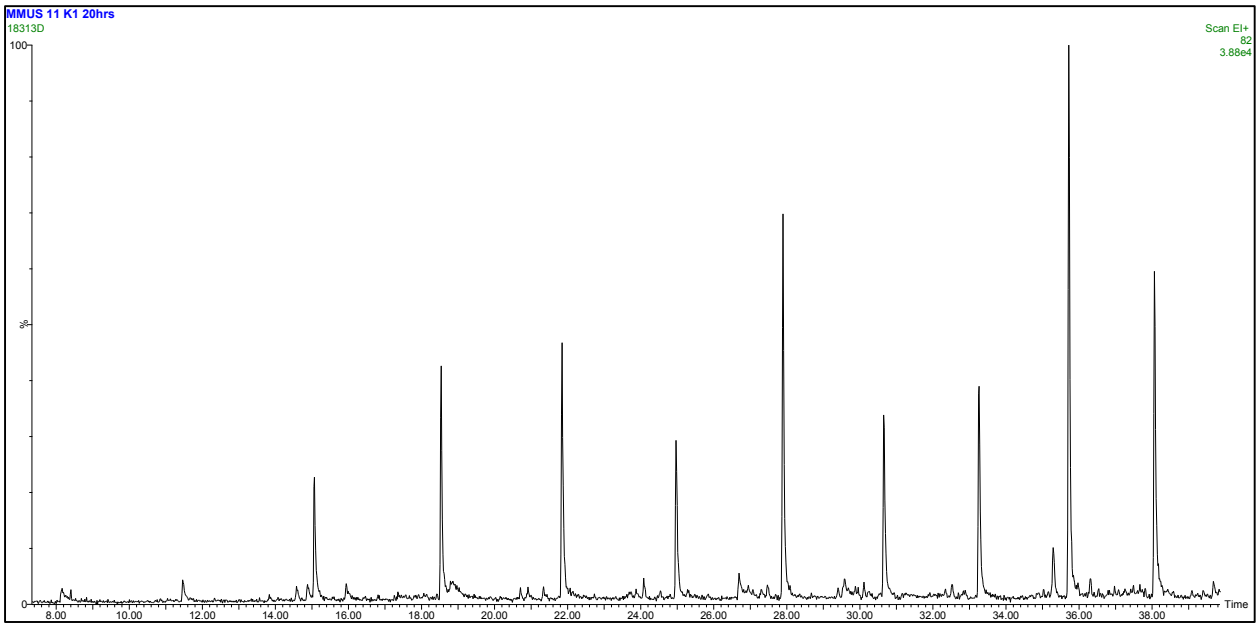


Figure: 3.22. A subtracted chromatogram of the sample F showing aldehyde homologue series.

Additionally, important chromatographic parameters like peak retention time (Figure: 3.22) and peak shape (Figure: 3.23), were used to add further confidence to identification of the unknowns. The polar functionalities, e.g. carbonyls (Figure: 3.23) are eluted in wider peaks due to increased interaction of the compounds with the stationary phase of the column. Decrease in polarity results in reduced interaction and sharpening of the peak shape, e.g. hydrocarbon sharp peaks (Figure: 3.24).

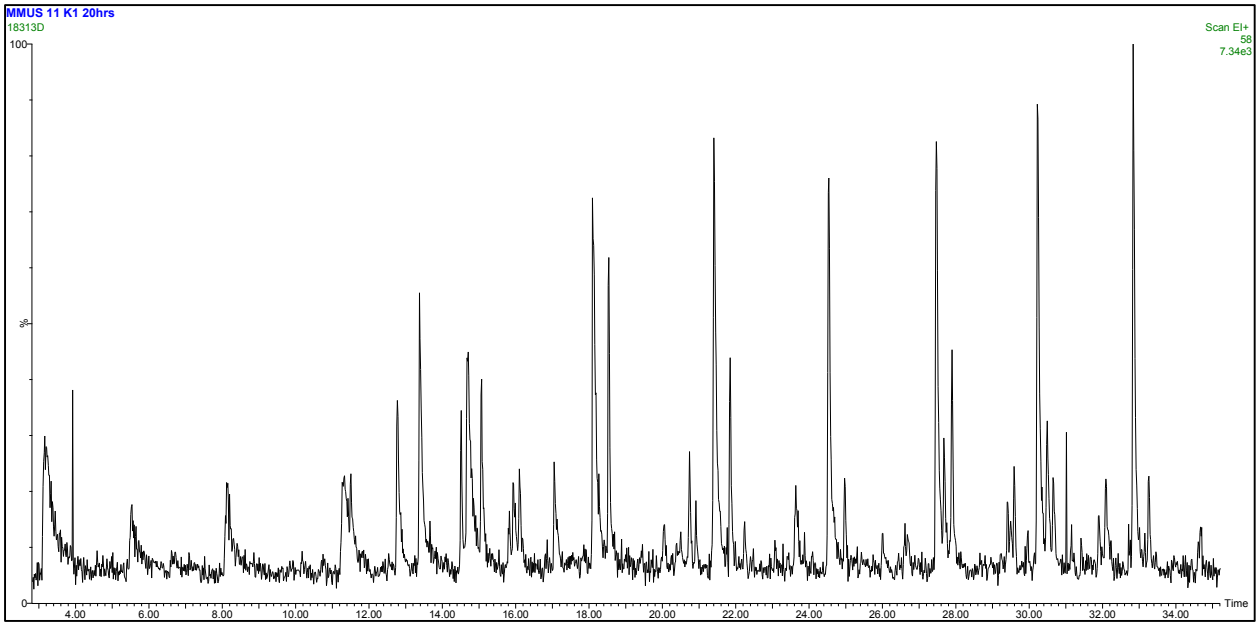


Figure: 3.23. A subtracted chromatogram of the sample F showing broad ketonic peaks.

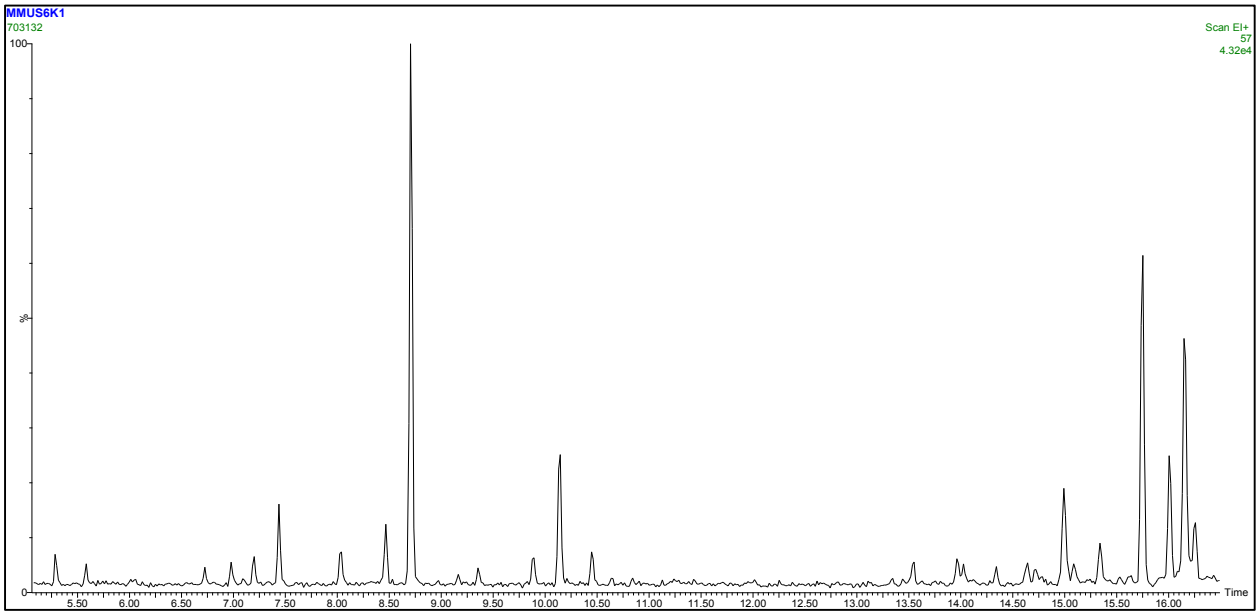


Figure: 3.24. A chromatogram of the sample C showing sharp peaks characteristic of hydrocarbons.

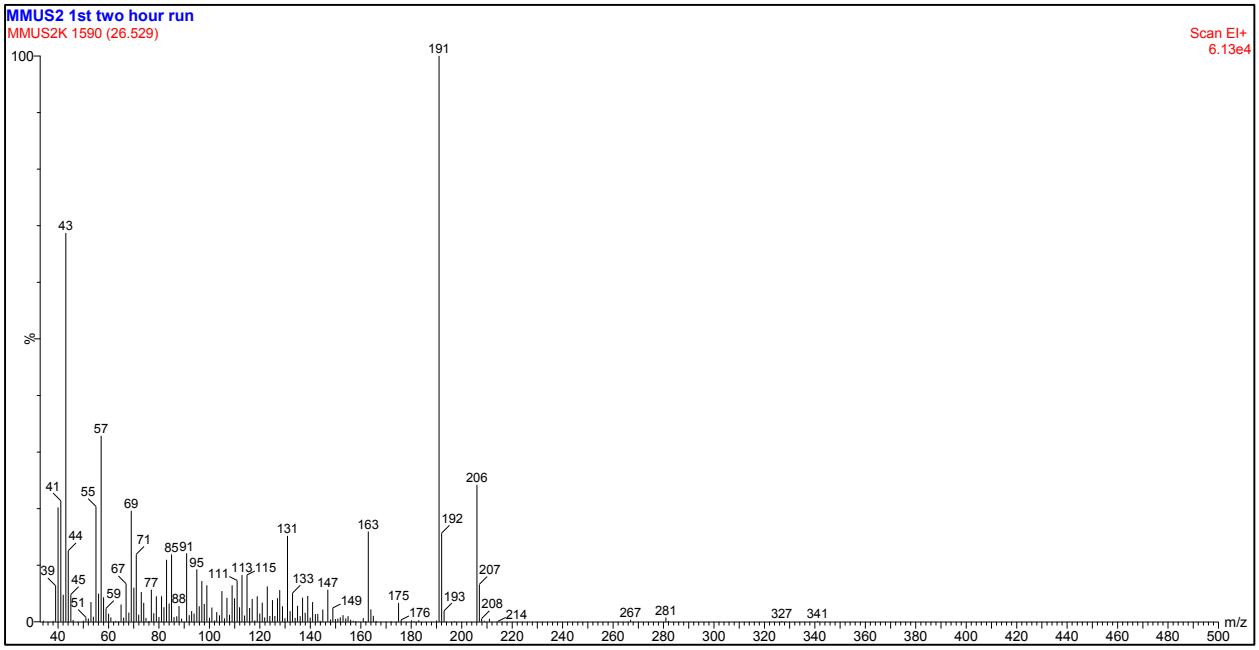


Figure: 3.25. Mass spectrum of a typical aromatic detected in samples with phenolic antioxidants.

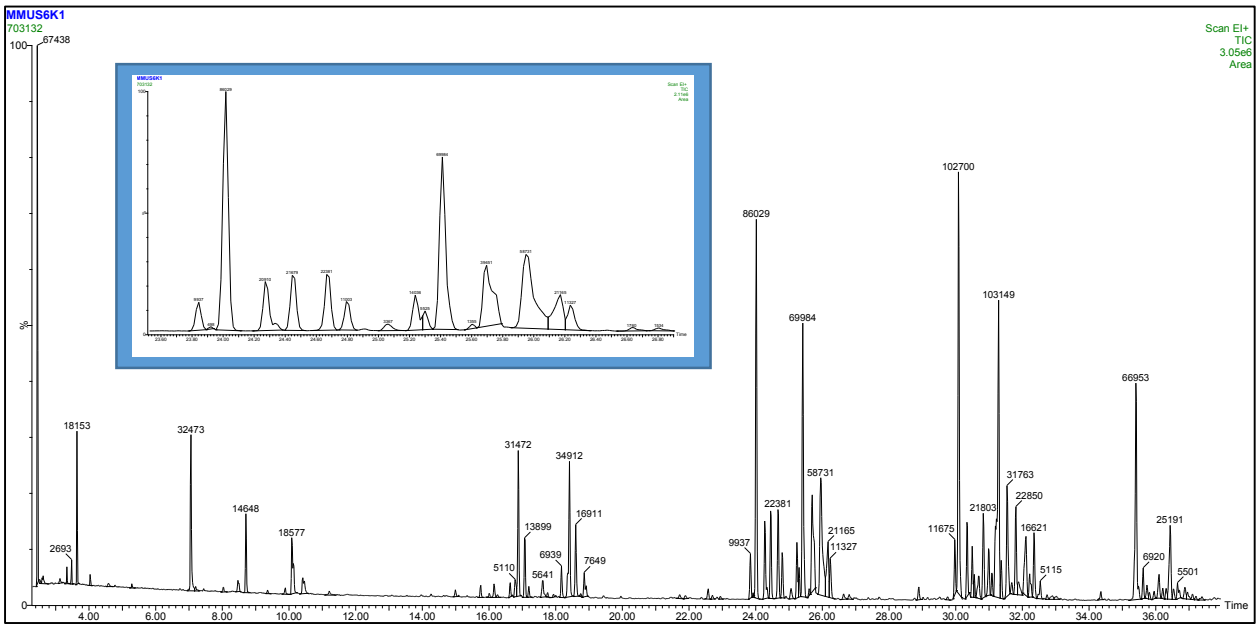


Figure: 3.26. A GC-MS chromatogram of the sample C, integrated for quantification.

The identification of the peaks in the TICs was followed by their quantification done using automated integration of the chromatograms that incorporated a fixed set of integration parameters (Figure: 3.17). The final data was represented as relative percent.

RESULTS AND DISCUSSIONS (CHAPTER: 4-6).

The results and corresponding discussion on the experimental work done in the current study is divided into three different chapters:

- CHAPTER: 4. ATR-IR ANALYSIS OF PP DEGRADATION
- CHAPTER: 5. CHEMILUMINESCENCE ANALYSIS OF PP DEGRADATION
- CHAPTER: 6. EMISSIONS ANALYSIS OF PP DEGRADATION

The division has been made to keep the discussion simpler and easier for the reader. Each chapter corresponds to an individual technique and discusses the PP degradation from a different perspective, as well as its correlation with the results from the other methods. The results in each section are discussed in the context of contemporary literature on thermo-oxidative degradation of PP.

CHAPTER: 4. ATR-IR ANALYSIS OF PP DEGRADATION

4.1. ATR-IR analysis of thermo-oxidative degradation of PP

Easy availability, simple operation and quick analysis makes IR spectroscopy a good choice for the investigation of thermo-oxidative degradation of polyolefins. Detectability of hydroxyl, carbonyl and alkene groups under an IR spectroscope makes the technique useful to study thermo-oxidative degradation analysis of polyolefins (Table: 4.1). The technique however, is limited in its sensitivity and has mainly been used to study the degradation process under accelerated aging conditions i.e. high temperature and prolonged ageing etc. The results of most of such studies did produce a fair representation of thermo-oxidative degradation behaviour of polyolefins, especially PP and PE, over a range of experimental conditions, e.g. in presence of air or nitrogen and at multiple ageing temperatures etc. The main drawbacks of such accelerated ageing experiments have been their inability to comment on the chemistry of the early stages of thermo-oxidative degradation and poor simulation of service life conditions of the polymer. In the current work, IR spectroscopy has been used to investigate early stages of thermo-oxidative degradation in solid-state of the polymer. The IR analysis conducted after ageing PP at 150°C in presence of air for up-to 2 hrs over a period of 24 hrs allowed a closer similarity with the real life conditions of the polymer in high temperature applications. The IR analysis under the conditions also made the corresponding results more suitable for a comparison with the emissions analysis that was also conducted under the same ageing conditions. The current chapter reviews the IR spectra of all PP formulations described in the Experimental Chapter (Table: 2.3-2.5). An attempt is made to assign the IR peaks to the possible functionalities. The temporal and thermal development of the IR spectra is used to explain underlying thermo-oxidative degradation chemistry. The IR spectra are also used to explain the stabilisation effect of the antioxidants packages on the degradation chemistry in the PP formulations.

4.1.1. Peak assignment of the IR spectra

The IR spectra of the formulations analysed in the current study exhibited obvious temporal development in hydrocarbon (2800-3100 cm^{-1}), carbonyl (1760-1665 cm^{-1}) the fingerprint (700-1500 cm^{-1}) regions of the spectra (Figure: 4.1). The extent of variation was significantly different across the formulations (Figure: 4.2-4.6). The hydrocarbon and fingerprint are generally the regions populated mainly with the splitting and bending vibrations corresponding to C-H bonds. Although, they generally contain information of limited scope for thermo-oxidative degradation

of the polymer, the variations in the two regions of the samples in the current study were too inconspicuous to be ignored. The carbonyl region, mainly due to its importance in the chemistry of thermo-oxidative degradation is considered the most important to be followed. All samples, except the sample B, D, E, G and O, showed significant changes in the fingerprint and the so-called hydrocarbon frequency region. There was a correlation between the observed variations in the spectra and the emissions generated by the formulations. It was observed that the formulations with more stable behaviour in these two regions also exhibited better control over headspace emissions (Chapter: 6) and CL emissions (Chapter: 5). The hydrocarbons therefore, can be assumed the majority product among the emissions as well as a significant proportion of the degradation products formed inside the bulk-polymer during its degradation. A cursory review of the IR spectra and the corresponding GC-MS and CL data revealed a general agreement among the results of the three experimental approaches.

As far as the carbonyl region is concerned, it comprises of a narrow frequency region populated by numerous peaks. The peak assignment therefore required a more comprehensive review of all spectra and their comparison. The peak assignment for all spectra (Figure: 4.2-4.6) along with corresponding reasoning used in their identification is reported in the Table: 4.2. Although distinction between the alcohol/acids spectra could be made easily, the assignment of the ester, aldehyde and ketones is somewhat blurred, and only best possible attempt could be made in making the assignment for these groups at this stage.

As one compares the spectra of the formulations, they appears divisible into the ones with alcohols and those with no-alcohols peaks in them. The non-alcohol formulations contained ester and aldehydes, instead. The former of the two groups was also the one with the formulations exhibiting weak stabilisation as also confirmed from the CL (Figure: 5.2-5.3) and the GC-MS (Figure: 6.2) data. Although the interference that could arise due to the potential absorption by the stabilisers or their degradation products did not cause much noise. No peaks for FS042 and SN1680, were observed in the spectra of the formations containing the two antioxidants [45, 122]. In some samples the typical carbonyl peaks widened significantly, e.g. sample H and F, the change in peak shape/peak area can be due to presence of multiple carbonyl groups, which appearing within short absorption window overlapped generating a relatively broader peak. This assumption was supported by the emissions for the respective formulations. It was observed that

the samples with broader carbonyl peaks, e.g. E and F, generated significantly higher aldehyde emissions.

In additional to the temporal variations in the qualitative and quantitative aspects of the IR spectra, the effect of the stabilisation packages was visible. In the Group: 1 formulations (Table: 2.3), for example, the formulations B-E (Figure: 4.2-4.3) showed a predominant emission of esters with relatively small extent of aldehydes. The synergic relation between hindered phenol + thioester combinations of the Group: 1 formulations was also evident in the GC-MS based emissions analysis (Figure: 6.2 and Section: 6.1.3). The carbonyl peak broadening was also observed for the formulation F, which also showed a high relative proportion of aldehydes among the emission made by the sample. Further, no aldehydes were observed among the emissions for the formulation G (6.1-6.3, 6.4-6.6), which also did not contain any carbonyl peaks in its IR spectra. The observation supported the presence of synergy between GA-80 and SN4120 (Table: 4.2 and Figure: 4.4) and better inhibition of the aldehyde forming oxidation routes, by SN1680 than FS042.

As far as the relative intensity of the IR absorption is concerned, lowest carbonyl absorption was observed for the formulation B, E and G, both containing a hindered phenol in combination with thioester and a phosphite, while the highest absorption was observed for the formulation A and F. The emissions form the formulation A were mainly a mixture of esters and ketones.

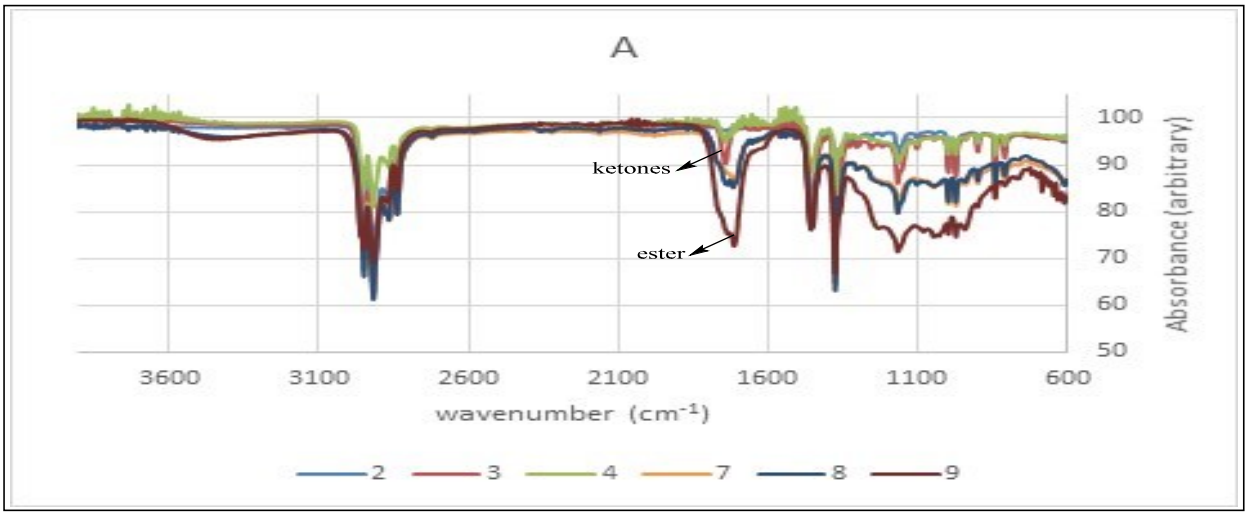


Figure: 4.1. IR spectral peaks of PP degradation recorded over 2, 3, 4, 7, 8 and 9 hrs of ageing.

An overview of the IR spectra of the Group: 2 formulations (Table: 2.4) showed the presence of carbonyls in the polymeric mass. All formulations in the Group: 2 contained FS042 instead of SN1680. It was observed that addition of hindered phenols into the formulations containing hydroxylamine reduced the extent of carbonyls. Further addition of thioesters into the formation containing hydroxylamine and hindered phenols, led to an increase in the extent of the carbonyls, demonstrating an increase in oxidative degradation of the polymer. In the Group: 3 formulations (Table: 3.5), the sample M and N showed relatively similar emissions both in qualitative and quantitative terms. The formulation O on the other hand, was far more stable It demonstrated a more slow and controlled development of IR absorptions corresponding to the carbonyl region.

Table: 4.1. Polypropylene infrared absorption bands in literature.

Functional group	**Sub-group**	**Frequency (cm^{-1})**
Hydrocarbons	alkanes	
		2850-3000 1350-1480
	alkene	
		3010-3100 675-1000 1620-1680
	alkyne	
		3300 2100-2260
Carbonyls	ketones	
	saturated ketone aryl ketone α,β-unsaturated ketone	1705-1725 1680-1700 1665-1685
	ester	
		1735-1750 1000-1300
	aldehyde	
		1740-1720 2820-2850 2720-2750
	acid	
		1700-1725 2500-3300 1210-1320

Table: 4.2. IR spectral assignments for the formulation A-O.

	a	b	c	d	e	f	g	h	
	1685 (amide)	1714 (acid)	2500-3360 (acid)	3200-3500 (alcohol)	1740 (ester)	2991-2829 (aldehyde peaks	1100-1300 (acid/alcohol)	1500-500 (fingerprint)	**comments**
A		*	*	*		*			b and d are characteristic of C=O and O-H for alcohols, the presence of an overlapped ketone cannot be ruled out either. Further, the over-all degradation appeared only after the first two hours of ageing, which is again in good agreement with the results of the GC-MS analysis for the formulation (Figure: 4.2).
B					*	*	*	*	e is characteristic of an ester which is further confirmed by the presence of two small peaks in the region g. Presence of aldehyde cannot be ruled out (Figure: 4.2).
C					*	*	*	*	more similar to the B except that the relative intensity is less than B. presence of ester cannot be ruled out (Figure: 4.2)
D					*	*	*	*	Both aldehydes and ester, the former being the main (Figure: 4.3).
E					*	*	*	*	Aldehydes and the ester, the latter being the majority (Figure: 4.3).
F		*	*		*	*	*	*	Ketones, acids, aldehydes, and esters, all possibilities are there (Figure: 4.3).
G									Both aldehydes and esters are the possible assignment the total intensity of the carbonyl peak however is significantly reduced relative to any other formulations (Figure: 4.4).
H	*	*	*			*	*	*	Acid is there, while the f indicates possibilities both for ketone and an amide, due to the presence of FS042 however, the f can be associated with an amid (the antioxidants peak). Aldehydes can also be a bleak possibility (Figure: 4.4).
I	*				*	*	*	*	Aldehyde/ester and amid (Figure: 4.4).
J	*				*	*	*	*	Aldehyde/ester and amide (Figure: 4.5).
K	*				*	*	*	*	Aldehyde/ester and amide (Figure: 4.5).

L	*				*	*	*	*	Aldehyde/ester and amide (Figure: 4.5).
M					*	*	*	*	Ester and alcohol are the possible assignments (Figure: 4.6)
N									alcohol is detected along with possibilities for the ester, and aldehyde (Figure: 4.6)
O					*	*	*		both aldehyde and ester are the possible assignments, alcohols and acids as well as ketones are excluded (Figure: 4.6)

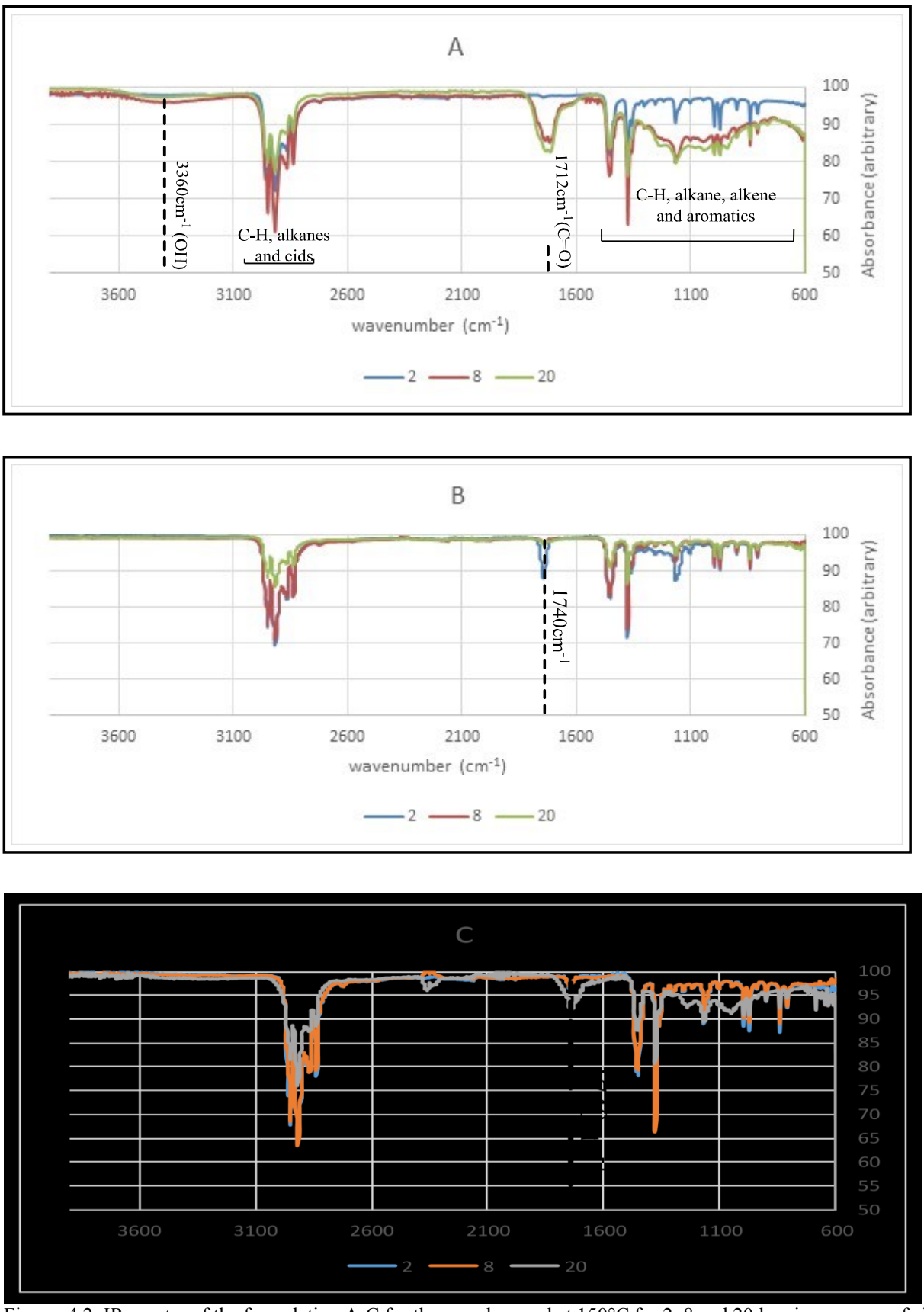


Figure: 4.2. IR spectra of the formulation A-C for the samples aged at 150°C for 2, 8 and 20 hrs, in presence of air.

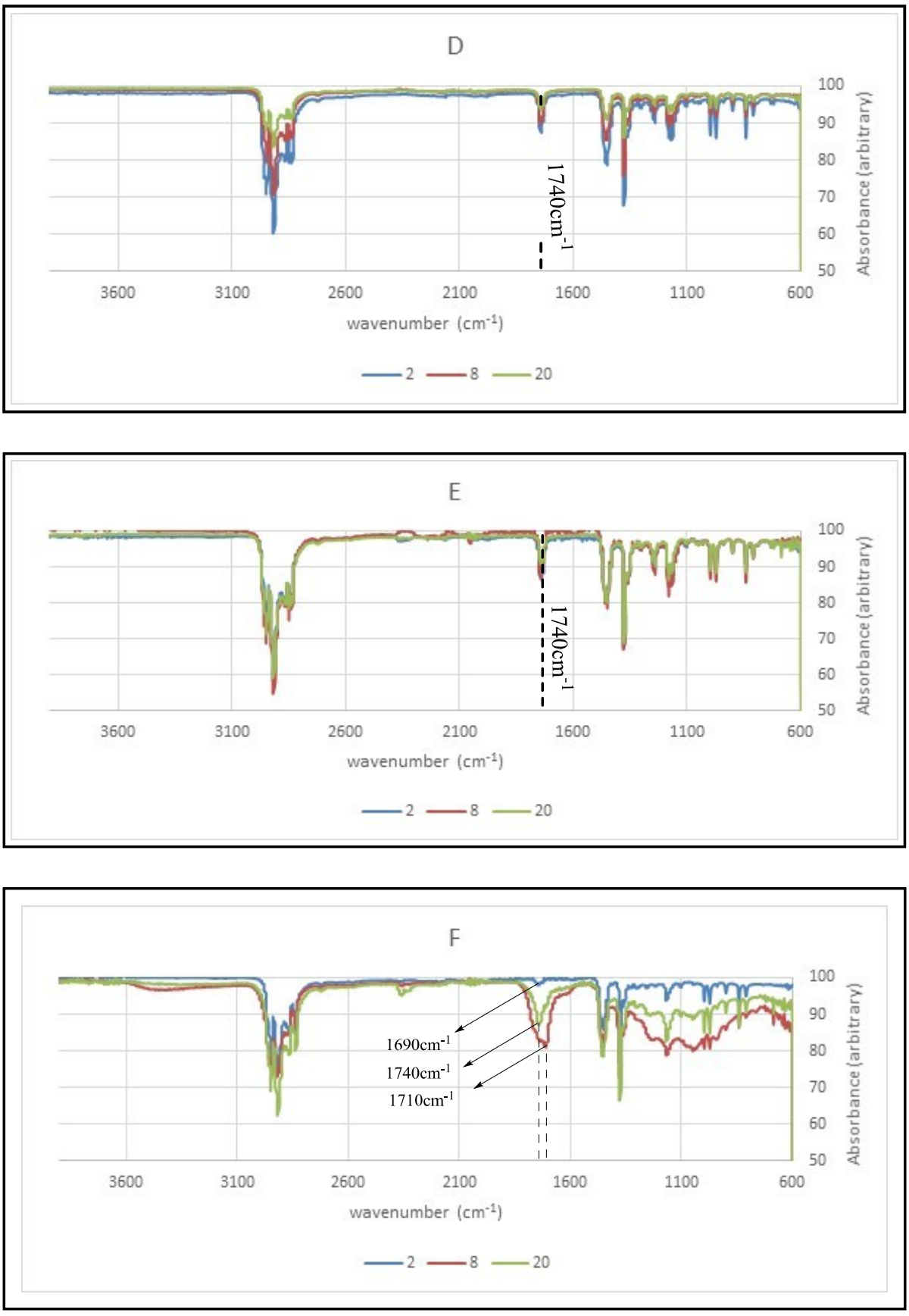
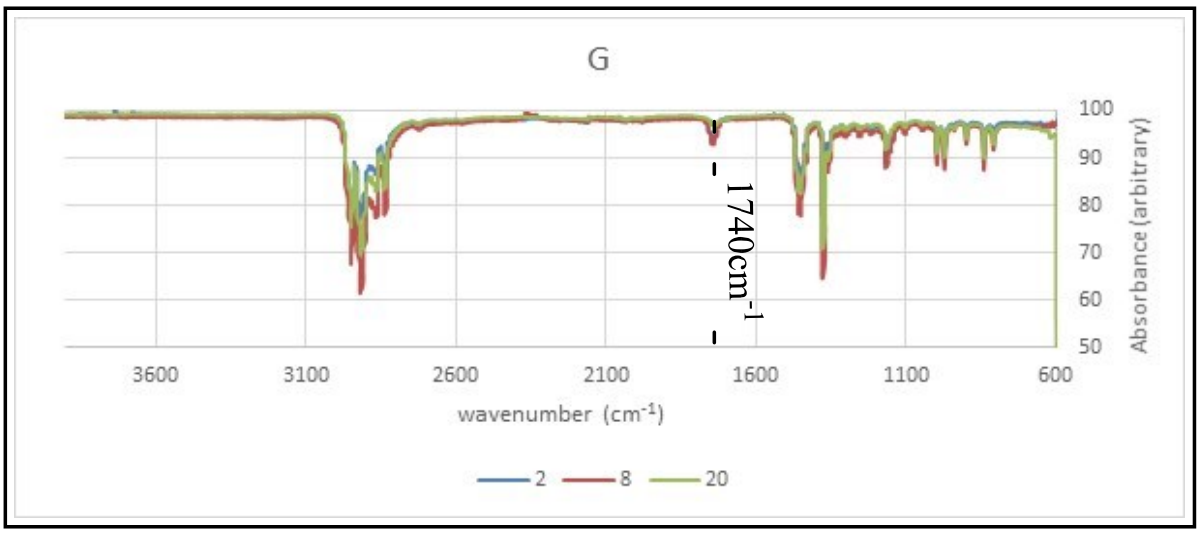
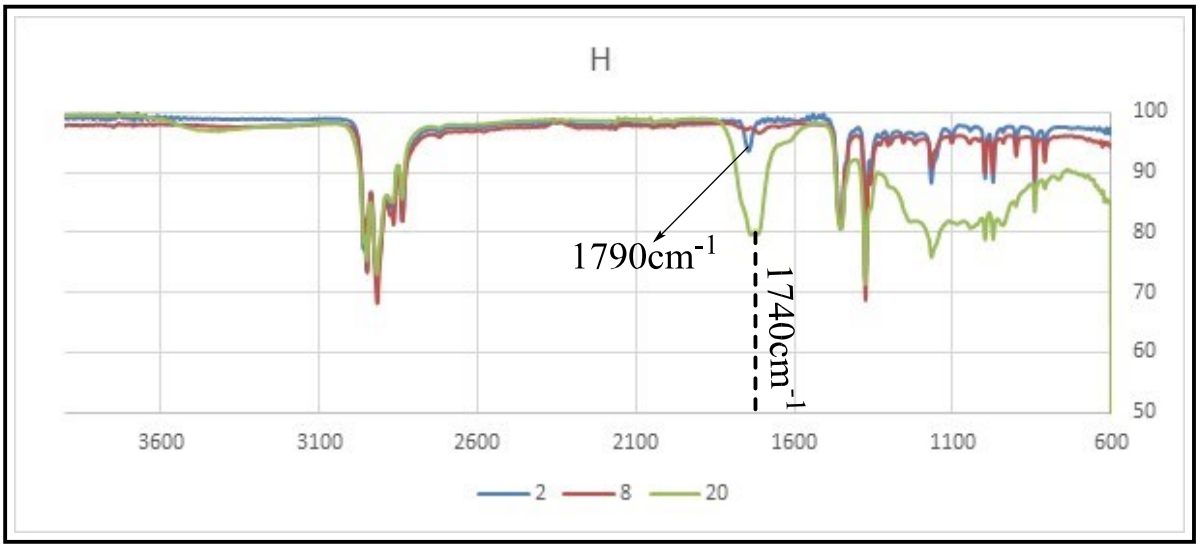


Figure: 4.3. IR spectra of the formulation D-F for the samples aged at 150°C for 2, 8 and 20 hrs, in presence of air.





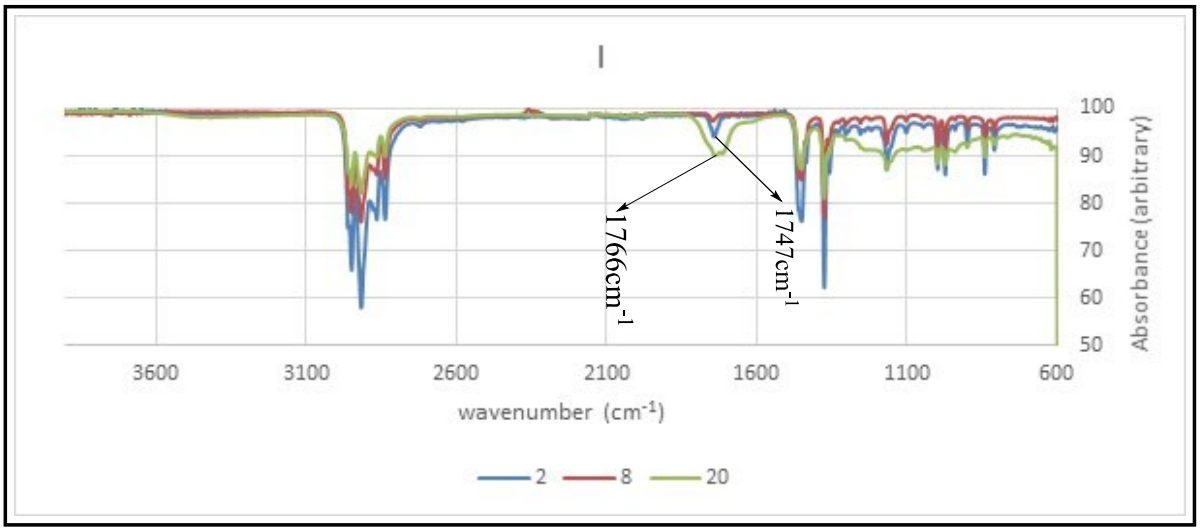


Figure: 4.4. IR spectra of the formulation G-I for the samples aged at 150°C for 2, 8 and 20 hrs, in presence of air.

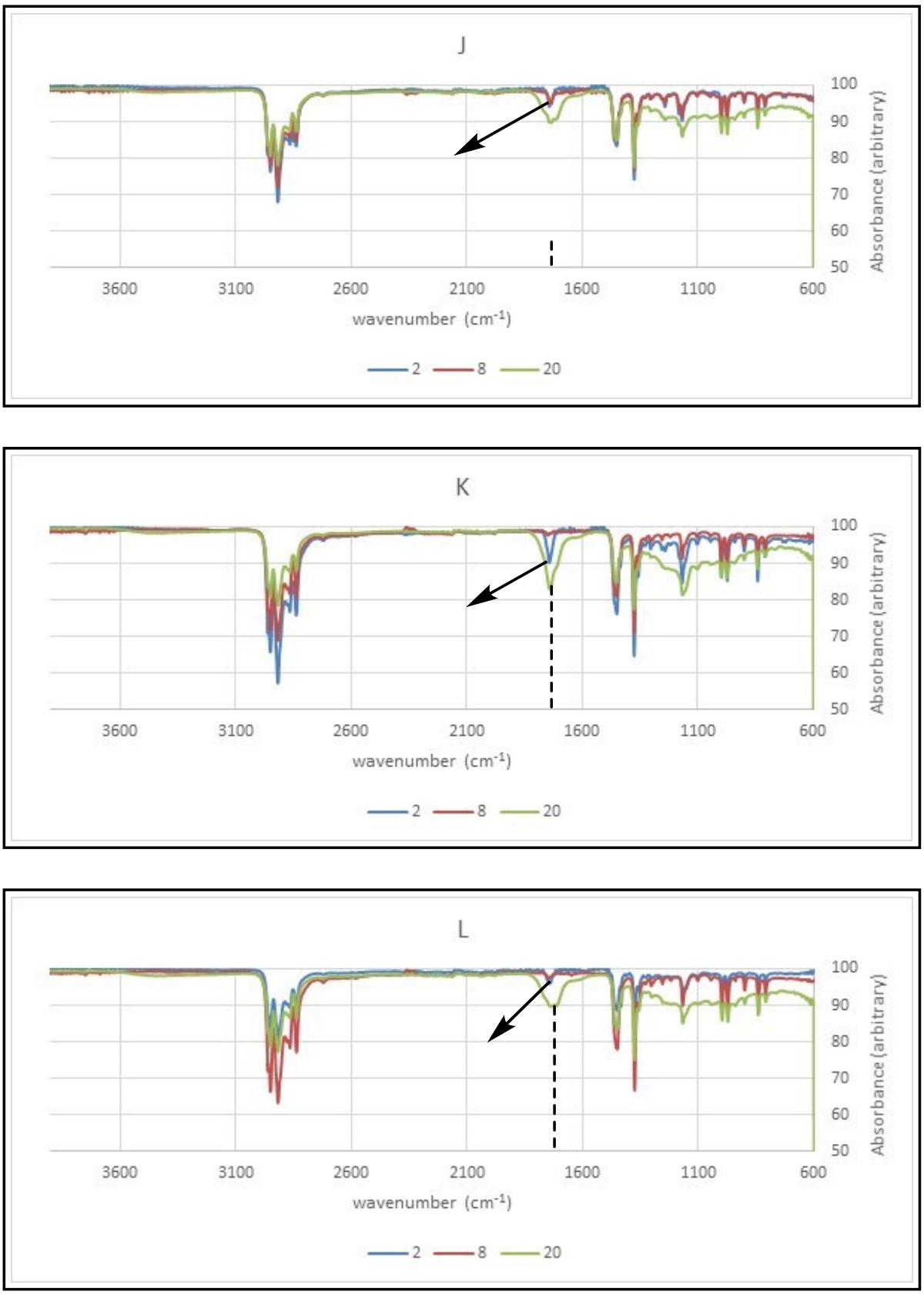


Figure: 4.5. IR spectra of the formulation J-L for the samples aged at 150°C for 2, 8 and 20 hrs, in presence of air.

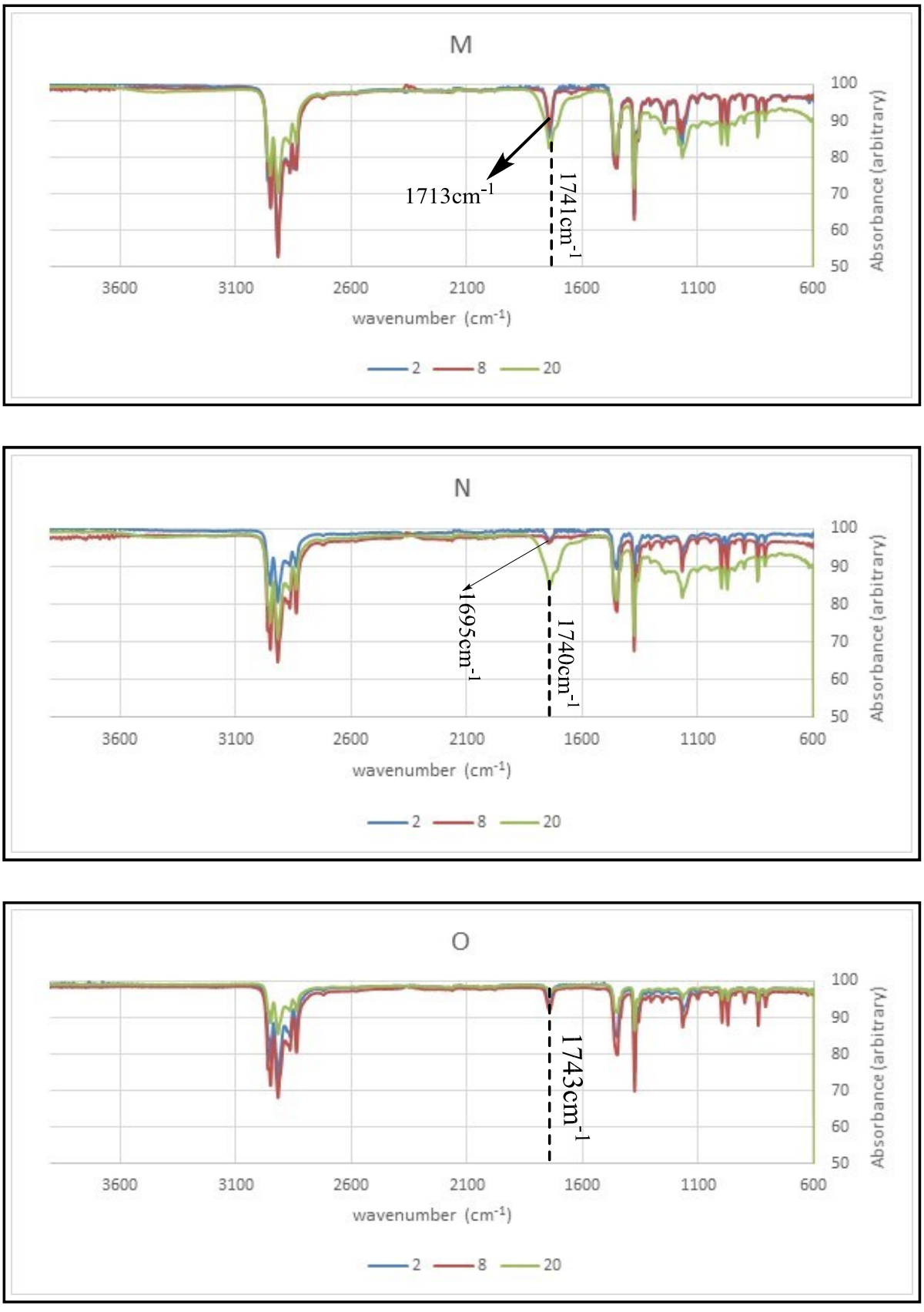


Figure: 4.6. IR spectra of the formulation M-O for the samples aged at 150°C for 2, 8 and 20 hrs, in presence of air.

Conventionally, quantitative aspects of IR spectra of polyolefin for thermo-oxidative degradation of the polymer are based on the calculation of carbonyl index for the carbonyl peaks in the spectra acquired over a range of ageing periods. The carbonyl indices plotted against time generate a curve representative of thermo-oxidative cycle of polymer degradation, typically a sigmoid curve with characteristic initiation, propagation and termination regions. For the current study the CI for all samples were calculated and observed to be non-zero at the zero ageing time. As shown in the Figure: 4.7-4.8, over the 20 hrs of ageing an increase CI in the range of 0.6-25 was observed among the samples, with a minimum for the formulation B and maximum for the formulation M.

The CI plots against time were unlike typical sigmoid curves representative of thermo-oxidative degradation cycle of PP, and different for different formations. In some formulations, there was a simple increase in the CI, while in the other an immediate decrease was observed (Figure: 4.7-4.8). Such a behaviours can be explained on the bases of the assumption that different formulations generated different carbonyl groups that subsided in their own way and time. Further, not all carbonyl groups necessarily developed in a linear way over time. The carbonyl index based on a particular carbonyl group therefore is hardly a litmus test for the phenomenon of thermo-oxidative degradation at its early stages in PP. The individual groups, within and across the formulations, therefore will be more useful to be treated separately. Tracing the development of ester and the ketonic peaks over time and among the formulations with different stabilisation packages seems more relevant to investigate the early stage of thermo-oxidative degradation in the solid state of the polymer by infrared spectroscopy.

To summarise the observation in short, thermo-oxidative degradation in the singly extruded stabilised PP formulations was observed in the form of esters aldehydes, ketones and alcohols that were generated during the 20 hrs of ageing. There was a temporal variation in the carbonyl content over time, and the nature of the carbonyl functionalities changed depending on the stabilisation packages. Even as early as 20 hrs of ageing, the solid-state polymeric formulations could be distinguished for the extent of thermo-oxidative degradation, which could be related to the stabilisation capacity of the stabilisation packages. Poor stabilisation packages were characterised by the formulations of alcohols, other than other groups, in the polymeric matrix, while the C-H regions (both in the fingerprint and in higher hydrocarbon regions i.e. 2700-2900 cm^{-1}) deteriorated significantly. Better stabilisation packages, e.g. C, G and O, showed

relatively weak ester peaks and a simultaneously better control over the C-H bands possibly associated with the hydrocarbons.

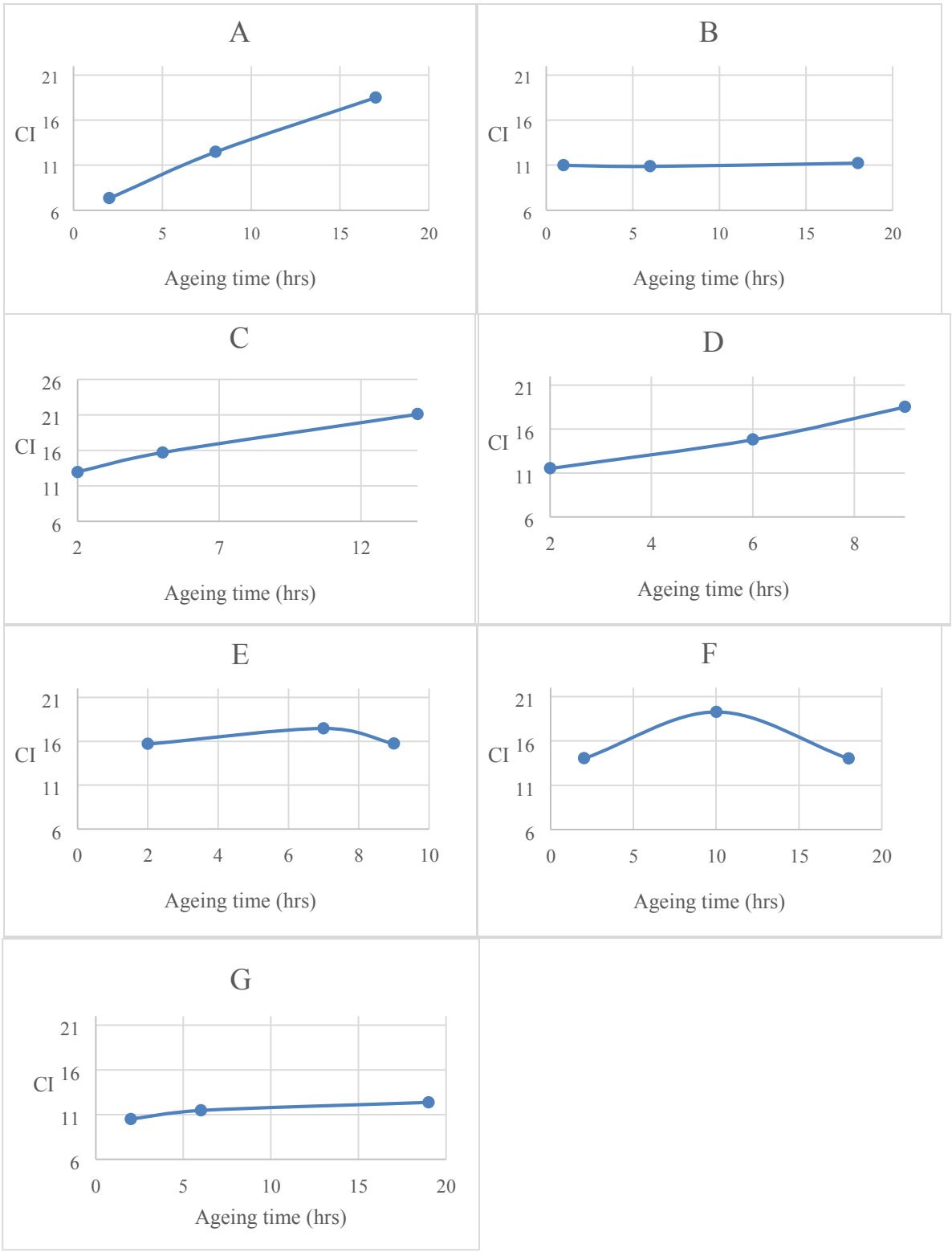


Figure: 4.7. Carbonyl indices of the formulations A-G plotted against time of ageing.

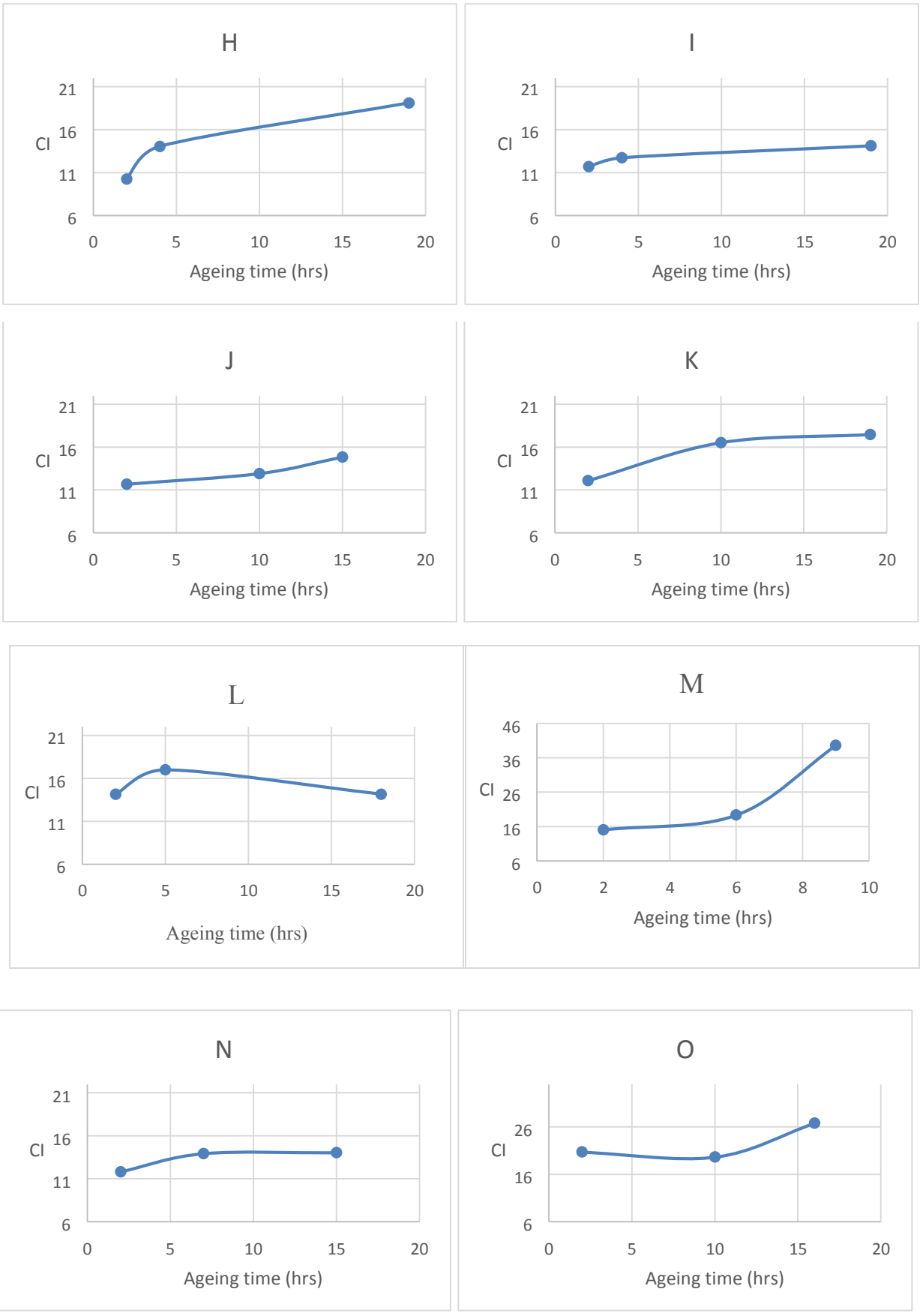


Figure: 4.8. Carbonyl indices of the formulations H-O plotted against time of ageing.

CHAPTER: 5. CHEMILUMINESCENCE ANALYSIS OF PP

Thermo-oxidative degradation of molten-state PP was investigated by CL spectroscopy. Analytical method and method optimisation for the CL analysis is explained in the Section: 2.3.2, and 3.2, respectively. The same samples that have been used in the IR analysis and the GC-MS emissions studies (Table: 2.3-2.5) have been analysed for their CL emissions. The samples have been analysed for the temporal evolution of the integral/total CL intensity emissions initially. The integral CL curves were further explored for the emission spectra to identify the emission wavelength for all samples. The integral CL emissions and CL emissions spectra are discussed in the current chapter in detail.

Although the integral CL emissions is a comparatively more established and conventionally adopted method of CL-based analysis it is only quantitative in nature. The CL emission spectra, despite their relatively recent introduction in the field of polymer chemistry and almost controversial nature as far as the exact assignment of the luminophores is concentred, do have potential to investigate chemical nature of the products of thermo-oxidative degradation. CL emission of polyolefins is generally a low intensity signal with and a low signal-to-noise ratio [85, 86, 90, 96]. The issue of typically faint CL emission from a polymer is commonly accommodated by allowing the emissions to be generated and accumulated for a pre-determined period before analysis. For the current study, the accumulation/interval between successive scans for the emission spectra was 10 min. Any integral and spectral CL data reported in the current section therefore, represent chemical changes expanding over a span of every 10 min. The CL intensity plotted against time gave integral CL curves (Figure: 5.2-5.4), which were resolved into individual spectra for the samples (Figure: 5.6-5.20). Before a more focused discussion on the CL data it important to describe some general characteristics that are of more general nature, and can be useful understanding the results better.

As reported in the contemporary literature, integral CL curve of un-stabilised PP is a typical sigmoid [83, 85, 86]. In the current study, since the polymer was analysed after adequate stabilisation a variation in the observed curve shape was inevitable. Despite the variation in the stabilisation packages, each curve had three distinct but common characteristics, which can be attributed to the three stages of the thermo-oxidative degradation cycle of PP i.e. initiation, propagation and termination (Figure: 5.1 and Figure: 5.2-5.4). As shown in the Figure: 5.1, the OIT region of each integral CL curve represents ‘initiation’, whilst the slope results from the

fast build-up of free radicals during 'propagation' and 'chain-branching'. Finally, each curve ended with a slight decrease and/or levelling-off in intensity, due to radical decay or termination.

A quick overview of the CL integral curves for the samples investigated in the current study shows that, it is mainly the OITs that changed across the formulations with different stabilisation packages. The curve regions corresponding to propagation and termination remained almost unchanged. Unlike the OITs, the difference in the maximum attained intensity (I_{max}) for the formulations has been comparatively insignificant (sample 'D' being the only exception). The integral CL curves were also the source of important CL parameters (Table: 5.1), e.g. oxidative induction time, emission intensity and the time to reach to maximum intensity. These parameters are useful to get an insight into the stabilisation capacity of the respective antioxidant packages, and mutual interactions between the various antioxidant groups.

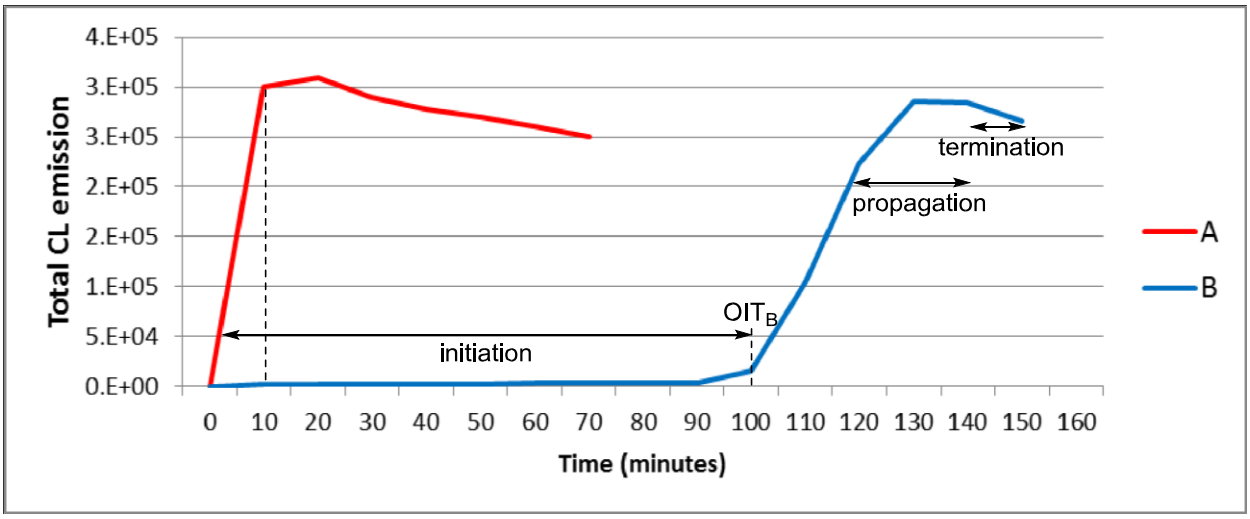


Figure: 5.1. Typical integral CL curves for stabilised PP formulation A and B (Table: 2.3).

Unlike integral CL emission curves the CL spectra of PP, and polyolefin in general, have not been investigated in literature very thoroughly. Poor CL emission and low signal-to-noise ratio were the challenges that have only been surpassed recently with the advent of better instrumentation. In absence of a definitive mechanistic explanation and spectral databases, it has been difficult to explain many spectral observations. In the current study, an attempt is made to assign the emissions bands to the possible luminophores. Temporal and thermal variations as well as the differences induced by the stabilisation packages of the formulations in the intensity

of the individual emission wavelength, is also used to explain underlying chemistry of the degradation in PP.

5.1. Integral CL emissions

Integral CL emission is a quick and simple way to study the development of thermo-oxidative degradation in a polymer, and stabilisation capacity of the antioxidants used in a polymeric formulation. The shape of a typical CL curve is not only a reflection of thermo-oxidative degradation cycle i.e. initiation, propagation and termination, but also a source of useful parameters (oxidative induction time, maxim intensity of CL emission etc.) for polymer degradation. Typical CL emission from polyolefin covers a wavelength range of 300-600 nm. The wavelength, according to the most establish mechanistic explanation, is associated with de-excitation of the triplet excited state carbonyls to a doublet state (Scheme: 1.19) [92, 95]. It is therefore a useful and direct tool to measure development of oxidation i.e. the formation of carbonyls, in polymers.

Like the discussion on the IR analysis (Chapter: 4) and the emissions data (Chapter: 6), the results of the integral CL emission analysis and the corresponding spectra are divided into three separate part corresponding to the three groups of PP formulations (Table: 2.3-2.5). The first group i.e. formulation A-G (Table: 2.3), was designed to explore the stabilisation effect of the hindered phenols and thioesters in presence of SN1680, a phosphite type processing stabiliser. The phosphite i.e. SN1680, primarily used as a processing stabiliser was unable to protect the polymer and showed almost instantaneous rise in the integral CL intensity. The zero OIT recorded for the formulation A (Table: 5.1) is the lowest among the formulations studied in the current work. The response recorded for SN1680 at this stage did not support its role as a processing stabiliser. The poor stabilisation of SN1680 in molten state of the polymer is justified by the active stabilisation zone for the antioxidant; as shown in the Figure: 1.2, the polymer is only suitable for stabilisation below the melting point of PP. In this backdrop, the so common use of the polymer as processing stabilisers need to be explored further.

In the Group: 1 samples, effect of hindered phenols on the stabilisation capacity of the phosphite was clearly demonstrated in the formulation B and C. Addition of two hindered phenols i.e. SN1010 and GA-80, increased the stabilisation of the formulation A (initially stabilised with SN1680 only) by 50 and 100 fold, respectively [27, 65]. A quick comparison among the formulation A, B and C, thus not only demonstrate a synergy between phosphite and hindered phenols, but also demonstrates GA-80 twice as better in stabilisation as the SN1010. The

synergy between the phosphite-type antioxidants and the hindered phenols has previously been associated with the higher consumption of SN1680 in the absence of a hindered phenol.

Table: 5.1. CL curves data for the samples A-G *(I_{max}; maximum intensity, t_{max}; time to reach the maximum intensity, OIT; oxidative induction time, PP; polypropylene).*

Chemiluminescence parameters: Group.1.				
I.D	Chemical composition	Imax	tmax	OIT
A	PP + CaSt. + SN1680	3.1×10^5	20	0
B	PP + CaSt. + SN1680 + SN1010	3.1×10^5	80	50
C	PP + CaSt. + SN1680 + GA-80	3.0×10^5	120	100
D	PP + CaSt. + SN1680 + SN1010 + DSTDP	1.0×10^5	60	50
E	PP + CaSt. + SN1680 + GA-80 + DSTDP	3.0×10^5	40	20
F	PP + CaSt. + SN1680 + SN1010 + SN4120	2.8×10^5	70	30
G	PP + CaSt. + SN1680 + GA-80 + SN4120	2.9×10^5	130	100
Chemiluminescence parameters: Group.2				
H	PP + CaSt + FS042	3.4×10^5	40	0
I	PP + CaSt + FS042 + SN1010	2.9×10^5	30	10
J	PP + CaSt + FS042 + SN1010 + DSTDP	3.2×10^5	30	10
K	PP + CaSt + FS042 + SN1010 + SN4120	3.0×10^5	40	20
L	PP + CaSt + FS042 + GA-80 + SN4120	1.4×10^5	40	30
Chemiluminescence parameters: Group.3				
M	PP + CaSt + SN1010 + DSTDP + vit. E	3.3×10^5	90	70
N	PP + ZnO + SN4120	3.6×10^5	50	30
O	PP + CaSt + SN1680 + SL1160	3.4×10^5	80	30

Although, any effect of the SN1680 on the stabilisation capacity or mechanisms of the SN1010 have not been documented in literature, the possibility of two-way chemical interactions cannot be excluded. Indeed, it will be useful to design a formulation with SN1010 or GA80 alone to be

able to make authentic comments on the question. Based on the thermally labile nature of SN1010, the absence of SN1680 can be expected to increase the degradation and subsequent emissions from the antioxidant further. The difference between the two hindered phenols: SN1010 and GA-80, in the formulation B and C, was very obvious. Although both stabilisers are good for adequate stabilisation of PP, GA-80 was twice as strong as the SN1010. The CL curves for the samples containing the two antioxidants was identical except for the length of the OIT region [45, 63].

Among the other factors that determine the strength of a hindered phenol is the number of hydrogens/protons/hydroxyl groups available in its structure. Since SN1010 has greater number of –OH groups, it is expected to be stronger than GA-80 (Figure: 2.1). However, other factors like thermal stability, molecular weight, physical mobility, solubility, and diffusion across a polymeric matrix need to be considered here. SN1010, for example, is almost twice as large in size as GA-80, which is likely to make its mobility through the polymeric matrix less. SN1010 is also more labile to thermo-oxidative degradation and loss of the subsequently formed fragments by evaporation leading to an indirect decrease in its active concentration available for stabilisation at a given point. The relatively higher degradation and volatilisation of SN1010 has also been confirmed by the analysis of the emission on the antioxidant itself and the formulation that contained the antioxidant. Multiple structures with features characteristic of SN1010 were identified, most of them with an obvious antioxidant character (Chapter: 7). The thermo-oxidative degradation observed for GA-80 was almost negligible when analysed under the same experimental conditions (Figure: 7.2).

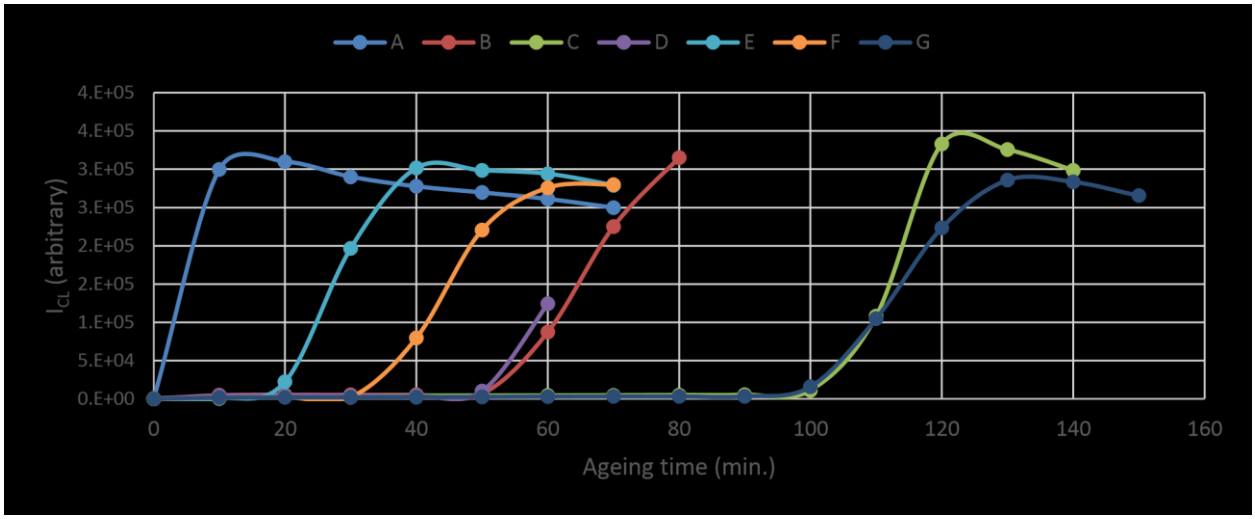


Figure: 5.2. Temporal evolution of total CL emissions from the formulations A-G (Table: 2.3).

Although strong stabilisers on their own, hindered phenols are commonly used in combination with other antioxidants of secondary nature. An important group of such secondary antioxidants is thioesters. For the current work, DSTDP and SN4120, two important thioesters, were tested for their effect on the stabilisation capacity of the hindered phenols in formulations with phosphites as the processing stabilisers. Although, in general, the thioesters did not appear to have any positive effect on the cumulative stabilisation, their interactions were not that simple. Addition of DSTDP to the formulation with SN1010 (B vs D), for example, kept the cumulative stabilisation unaffected, while a decrease was observed when the DSTDP was replaced with SN4120 (D vs F). Unlike SN1010, a positive interaction was observed between the GA-80 and SN4120, and a negative between the GA-80 and the DSTDP. The prevalent idea of synergy between the two groups i.e. hindered phenols and thioesters were not demonstrated as a general principle in molten state polymer. As one compares the CL behaviour of the formulation D, G and E, F with the emission data for the formulations, it becomes evident that relatively higher CL emission for the formulation E and F is related to the higher aldehyde based emissions generated by the two formulation. The aldehyde emissions was observed at as low temperature as 90°C and consistently increase thermal and temporally in the two formulations, The same emissions therefore, are more likely to increase in the molten state of the polymer.

Upto this stage it was evident that SN1680 does not have any stabilisation effect for PP in molten state of the polymer. The next question that arises at this stage is that does it have any effect on the cumulative stabilisation capacity of the hindered phenols and thioesters ? To answer this question, a new set of formulations was designed by replacing the SN1680 with FSO42. It was expected that by discarding the FS042 the effects that can be associated with SN1680 could be discerned. FS042 is a hydroxylamine that is active in the same thermal range as SN1680, however, unlike the phosphite, it works in an over-stoichiometric manner by recycling itself through a cyclic stabilisation process, hence expected to be available in the polymeric matrix for prolonged period without additional effect generated by the presence of a hindered phenol. In the current study, FS042, at its own, demonstrated better stabilisation of PP than SN1680. The OIT of the formulation increased ten folds in comparison with the SN1680. The effect of the hindered phenols (SN1010 and GA-80) and thioesters (DSTDP and SN4120) toward a cumulative stabilisation effect, in presence of FS042 as the processing stabiliser however, was half of what was observed in the Group: 1 formulation with SN1680 as the counterpart. It was also observed that, unlike Group: 1, SN4120 was an equivocal synergist

toward the hindered phenols i.e. it increased the stabilisation capacity of both SN1010 and GA-80.

The third group of the formulations was of a distinct composition as it had the CaSt replaced by ZnO (N), and a light stabiliser i.e. SL1190 was used in combination with SN1680 (O). Also vitamin E was tested (M). Although the addition of vitamin E has a positive effect on the cumulative stabilisation of a formulation containing SN1010 and DSTDP, it will be interesting to investigate the Vitamin. E in multiple other formulations. Basically Group: 3 need to be further studied by designing more combinations of the antioxidant packages. This aspect is elaborated in the 'Further work' (Table: 8.1).

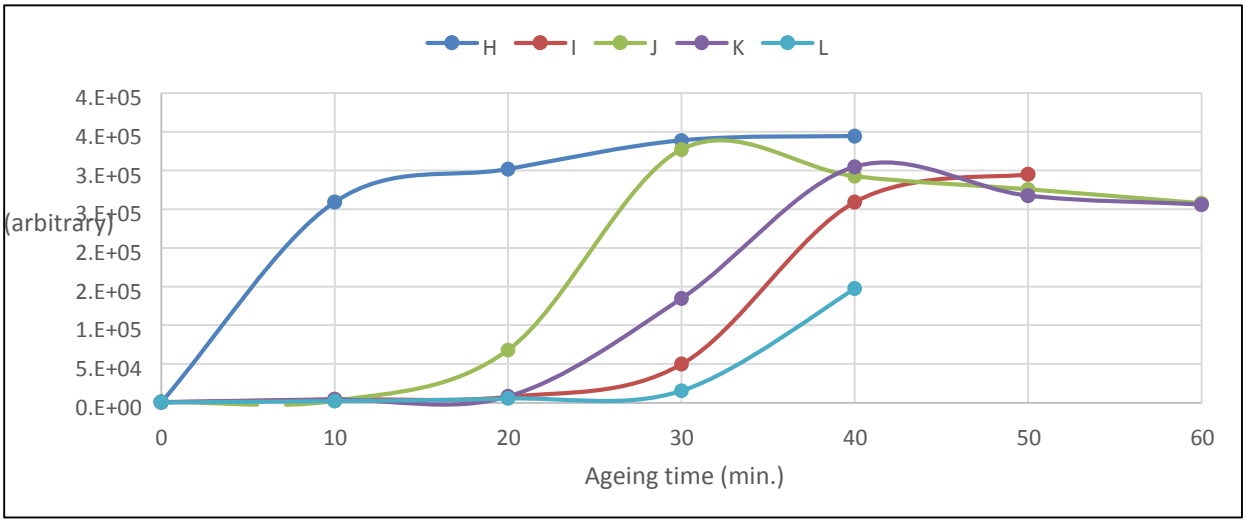


Figure: 5.3. Temporal evolution of integral CL emissions from the formulation H-L (Table: 2.3).

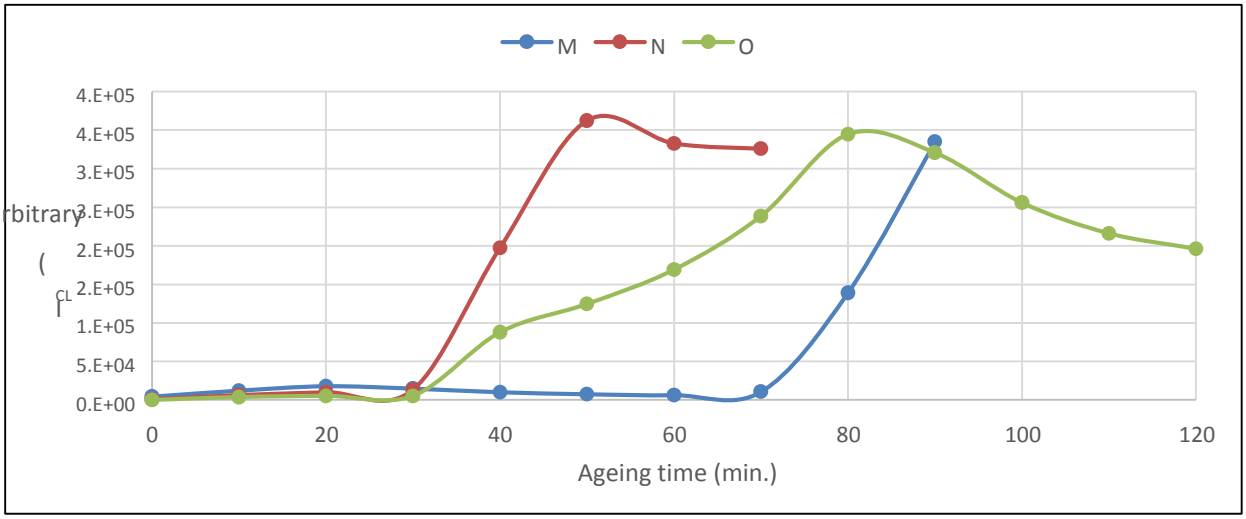


Figure: 5.4. Temporal evolution of integral CL emissions from the formulations M-O (Table: 2.4).

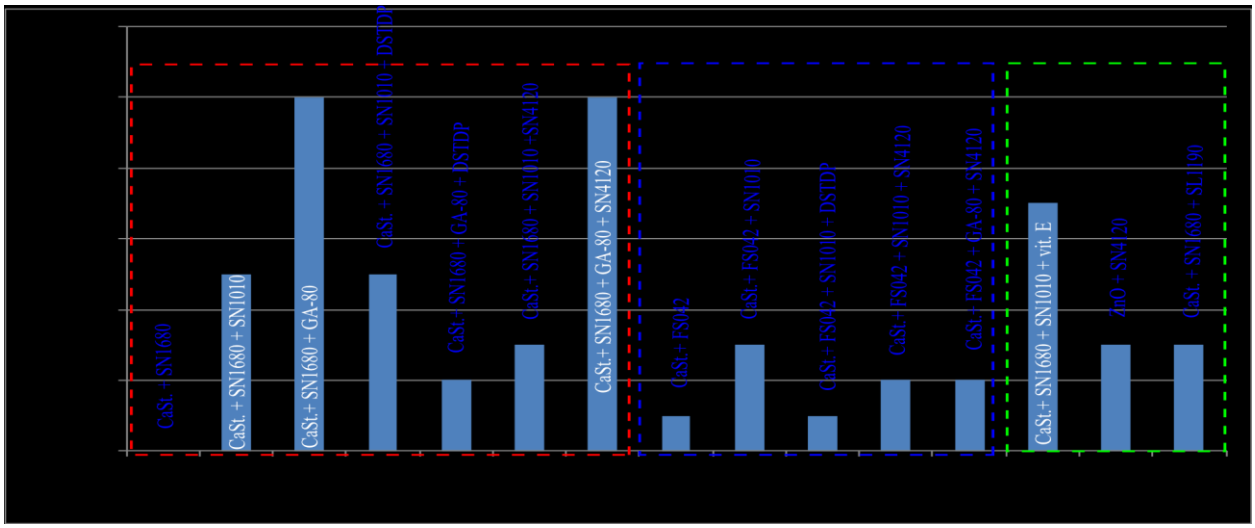


Figure: 5.5. Comparison of oxidative induction time of the formulations A-O.

To conclude the current section, CL integral analysis has been used to investigate stabilisation and interactions among various groups of antioxidant, better as well poor performing combinations are highlighted for a range of important polyolefin-based stabilisers. Based on the result some further formulations are suggested. Through a comparison of the CL integral curves based data and the GCMS based results of general emissions it have been shown that, unlike previously over-emphasised role of ketones, aldehydes have been put forward as important candidate incorporating to the CL-based emission from stabilised PP. This proposal also gains strength from the significantly reduced ketone based emissions from the formulations with low OITs and corresponding CL data.

5.2. Chemiluminescence emission Spectra

The integral CL curves are quantitative in nature and pertain to overall CL emission from an ageing sample. Not much can be said about the chemical nature of the species that generate the integral CL signal, for a given formulation at this stage, except that they are carbonyl compounds or oxidation products of the polymer. The emission spectra of the CL-active species were acquired to fill this gap. Unlike conventional spectroscopic methods, the CL spectra are not live scans, rather a polymer is allowed to age and the degradation species are allowed to accumulate before they can be scanned for an emission spectrum. A CL spectrum, therefore, is a combination of the spectra acquired over the various intervals of time, typically every 10 min The emission spectra for the current work were acquired in the range of 300-700 nm. In all formulations, the negligible emission below 400 nm and above 600 nm was in agreement with relevant literature. Like un-stabilised PP, the spectrum for each sample appeared as a single broad band. Unlike the same however, it was interspersed with some fine structure, probably, corresponding to different CL-emitting groups (Table 5.2).

Previously, only 1-3 bands (410 nm, 440 nm and 490 nm) have been reported in the CL emission spectra of PP. In the current work however, the number increased to five prominent bands including 420 nm, 460 nm, 480 nm, 560 nm, and 600 nm (Table: 5.2) [92, 95]. The increase in number of the bands can be due to the high ageing temperature, presence of stabilisers, or the result of the formation of secondary degradation products resulting from interaction among primary carbonyl groups previously reported [77, 84].

In general, the CL analysis did demonstrate a correlation with the IR results in the sense that heterogeneous and dynamic nature of the oxidative degradation products was observed at various stages and among the formulations. The integral CL curves also provided a guide-line to back the work on emissions to be conducted at latter stage. Many of the observation extracted from the CL analysis were strengthened by the results of the general emissions as reported in the next section of the current report.

To begin with the first group of the formulations i.e. A-G (Table: 2.3), six different peaks i.e. 420 nm 460 nm, 480 nm, 560 nm and 600 nm were consistently detected. Among these peaks 420 nm, 460 nm and 500 nm can be considered the red shifted forms of the 410 nm, 440 nm and

490 nm assigned in literature to isolated carbonyls, conjugated carbonyls, and α, β-unsaturated ketones. The apparent shift in the wavelength of these three bands can be attributed to the variation in the experimental parameters, e.g. temperature at which the polymer was analysed. The intensity of the peaks has been observed to be relatively low and more evenly distributed during the initiation phase of degradation. During propagation however, the spectra were blue-shifted with the 420 nm as the most prominent peak. During termination the spectrum was again red-shifted with 500 nm as the new centre of the spectra in general [84, 92].

Table: 5.2. CL emission spectral bands for the stabilised PP formulations A-G [84].

CL emission bands for the formulation A-G		**Sample i.d**						
Λ (nm)	**Luminophore**	A	B	C	D	E	F	G
420	Isolated carbonyls	*	*	*	*	*	*	*
460	Multiple carbonyls	*	*		*			*
480	Conjugated carbonyls			*		*	*	
500	α,β-unsaturated ketones	*	*		*	*		*
560	Unknown	*	*	*	*	*	*	*
600	Long conjugated carbonyl	*	*		*	*	*	*
CL emission bands for the formulations H-O		**Sample i.d**						
nm		H	I	J	K	L	M	N	O
420	Isolated carbonyl	*	*	*	*	*	*	*	*
460	Multiple carbonyls								*
480	Conjugated carbonyls	*	*	*	*	*	*	*	
500	α,β-unsaturated ketones								*
540	?	*							
560	Unknown		*	*	*	*		*	*
600	Long chain conjugated carbonyls							*	*

As far as the nature of the peaks is concerned, except for the extra peaks that that can be due to the antioxidants especially the thioesters, a general agreement with literature was evident. The temporal variations in the peaks, e.g. 420 nm and 500-and-above, were slightly different from the trends generally reported in literature. Like many other works in the literature, for example, the peak at 420 nm was the main peak during the propagation phase of an integral CL curve, and

high peaks i.e. 500 nm and above, started to appear in a comparative intensity toward the termination of CL-decay end. Unlike the trends reported in literature reporting a clear red shift in the spectra the relative variation in the intensity of the lower i.e. 340-520 nm, and the higher region of the spectra i.e. 420-520 nm, however, was more comparative and getting to a rather even distribution in many cases (Figure: 5.6-5.20).

According to spread model of thermo-oxidative degradation, the 420 nm band corresponds to carbonyl build during early and fast growth of thermo-oxidative degradation, which continuous until the particular area is completely oxidised. A red shift in the spectrum after the intensity maxima, complete oxidation of a region according to the spread model, is actually either due to absorption and re-emission of the CL photons by the species in the oxidised region, or consequence of the formation of longer chain and conjugated carbonyl. The spread model is mainly based on the slow diffusion of the ready-oxidised species consequently infecting other more vulnerable area in a polymer, does not necessarily holds true for a molten state sample where the hindrance to mobility is surpassed to greater extent. Ironically the same explanation holds for the diminishing of the red shift reported in the works based on the solid polymer [93].

A quick review of the CL emission spectra (5.6-5.12) shows the bands as distinct wavelengths. A regular pattern in which various particular emission bands appear in various region make the spread model, e.g. 420 nm appearing in the propagation region, a model based on physical spread affecting the wavelength of the emission bands, less likely an explanation within which they can fit. Further, in a molten polymeric formulation as the ones analysed in the current study, oxidation species are more free to diffuse through and less abstracted by physical state and sample geometry. Also there are examples, e.g. formulation A in the Figure: 5.6, where both the lower and the higher wavelength region sustain a comparable intensity throughout the propagation region. From a formulation like ‘A’, based on the spread model based red-shift idea, one should expect a pronounced red shift in the spectrum. A comparison with the GC-MS based emission again provide a corroboratory evidence, by showing that ‘A’ emits all sort carbonyl-based groups in comparative abundance. The approach that different chemical species are formed at various stages of thermo-oxidative degradation appears to be more logical explanation of the experimental evidence acquired so far. Another interesting example is the formulation O, as shown in the Figure: 5.20, it appears to be consisting of two twin spectra growing rather independently of each other.

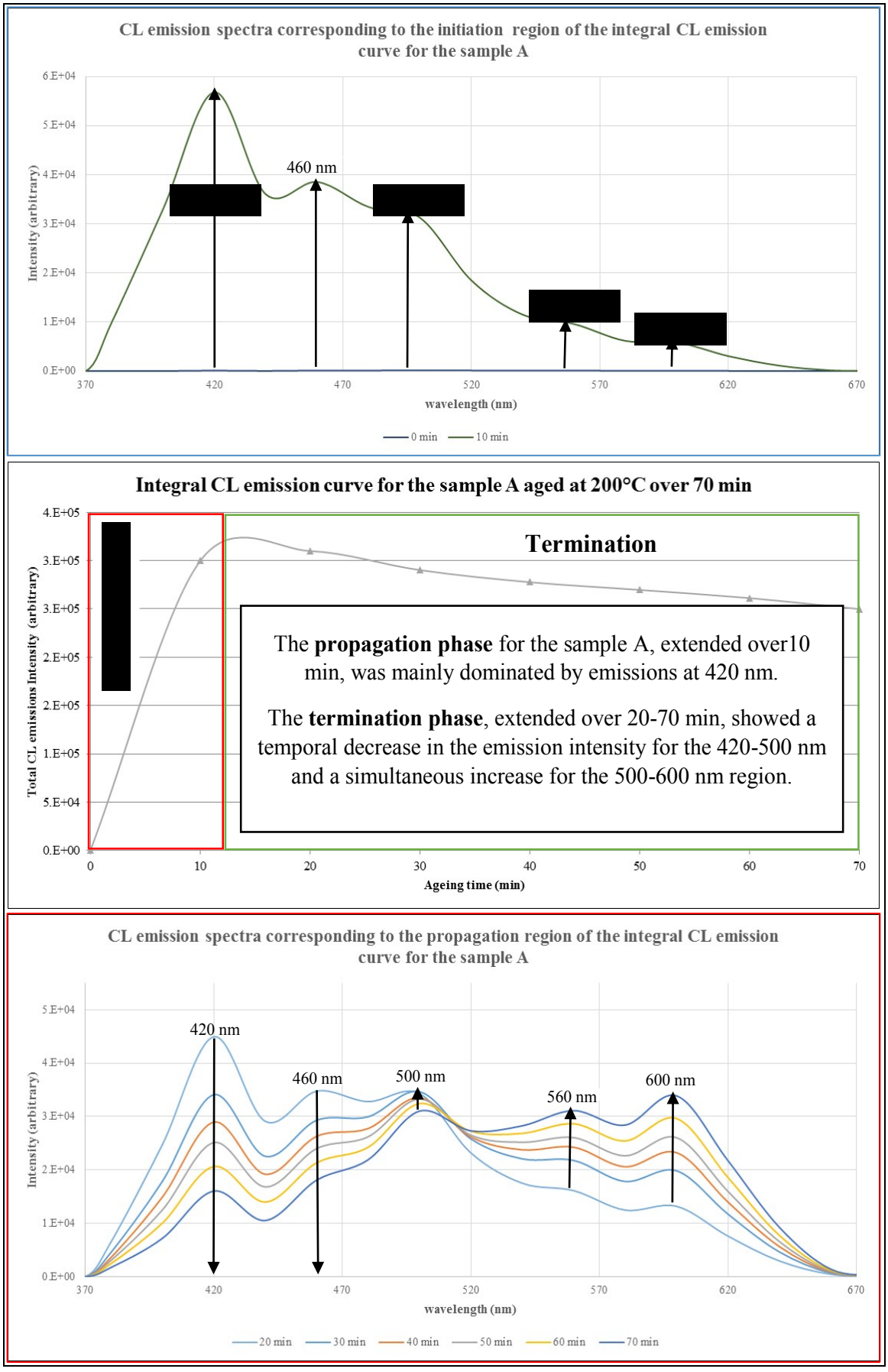


Figure: 5.6. Integral CL curve and corresponding spectra for the formation A.

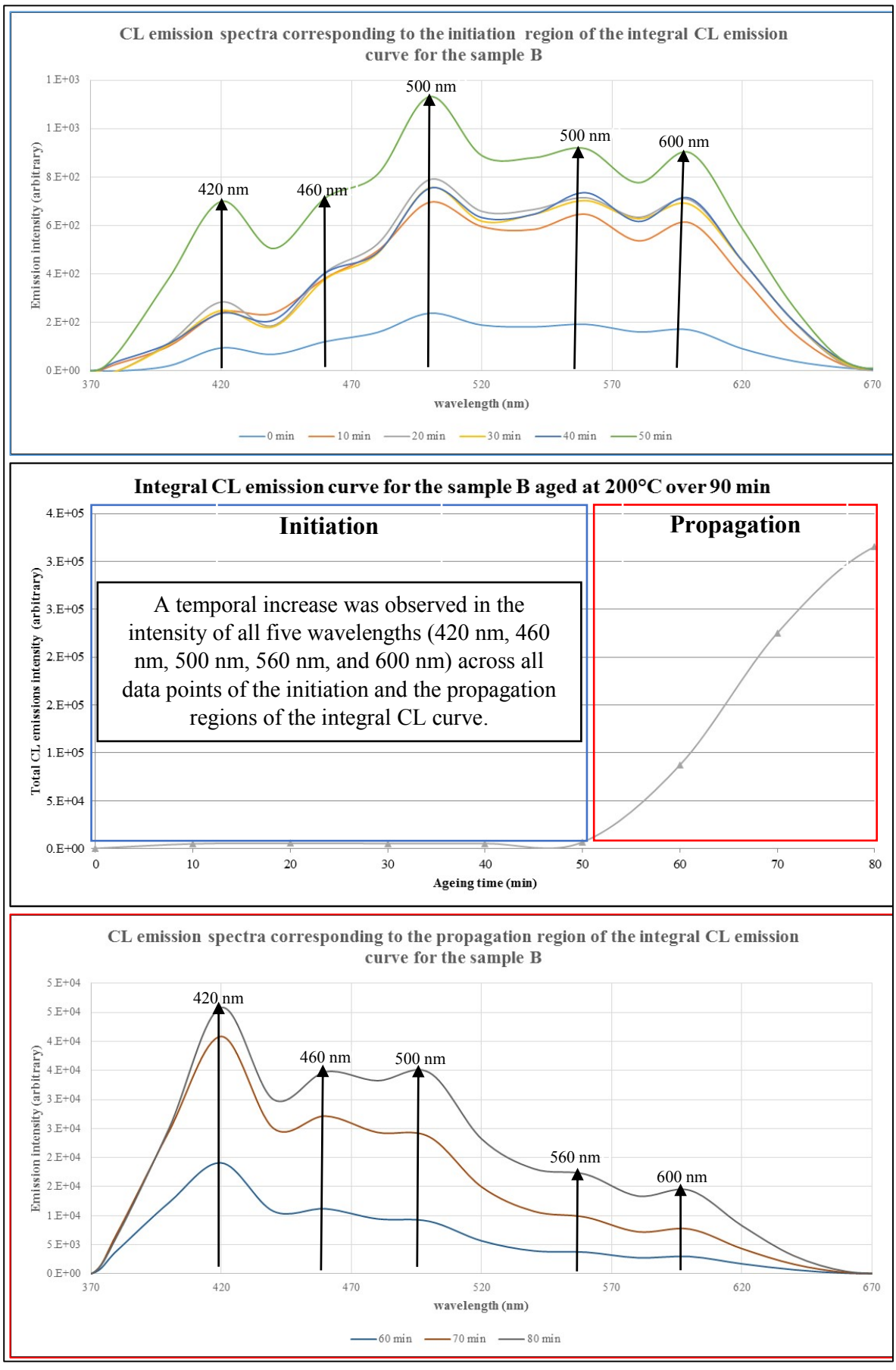
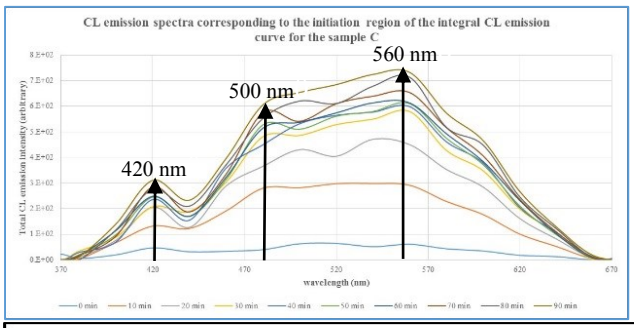
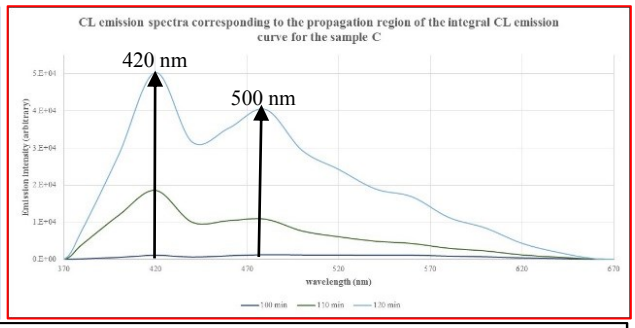
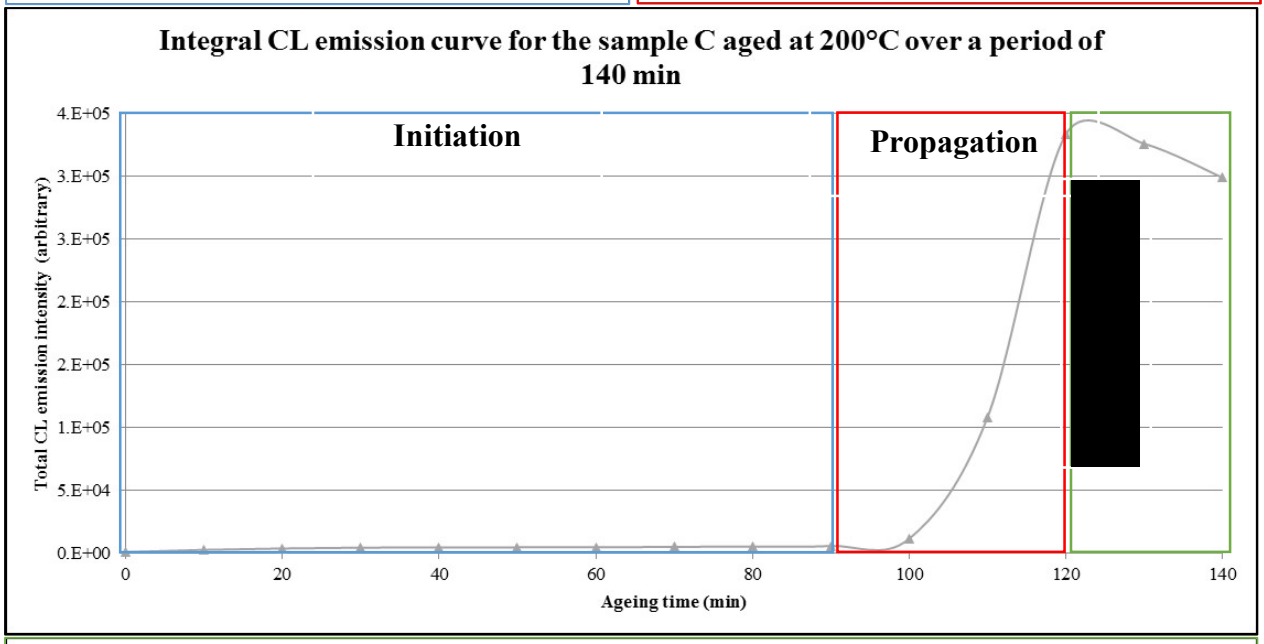


Figure: 5.7. Integral curve and corresponding spectra for the formation B.







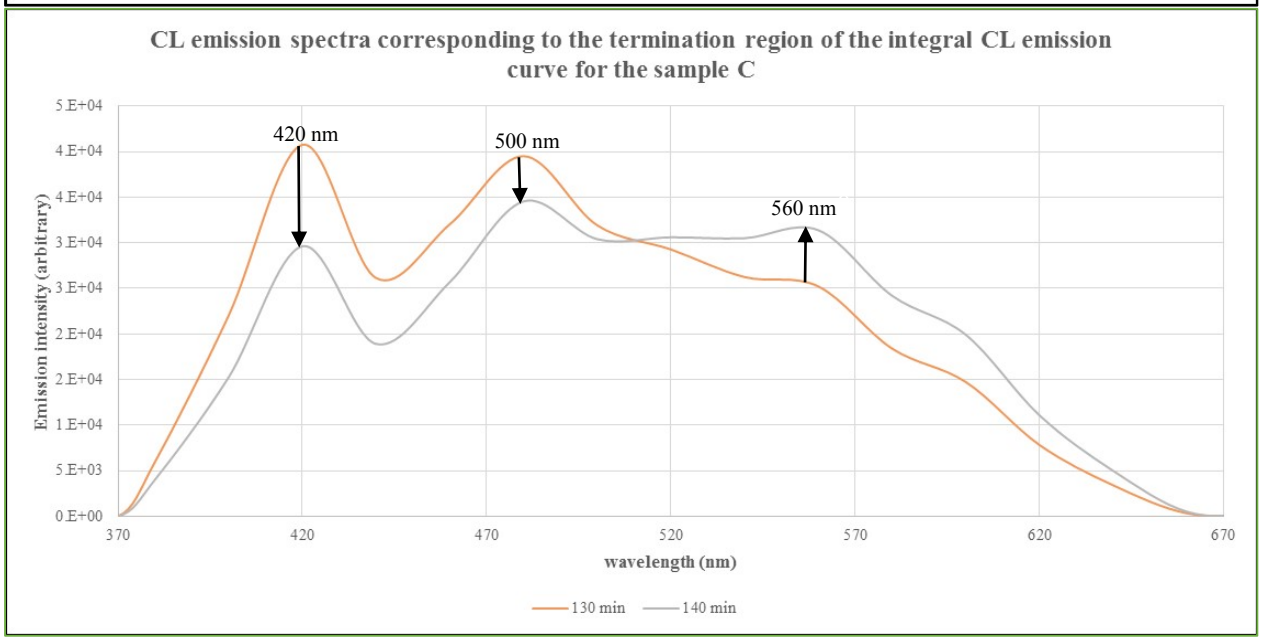


Figure: 5.8. Integral CL curve and corresponding spectra for the formulation C.

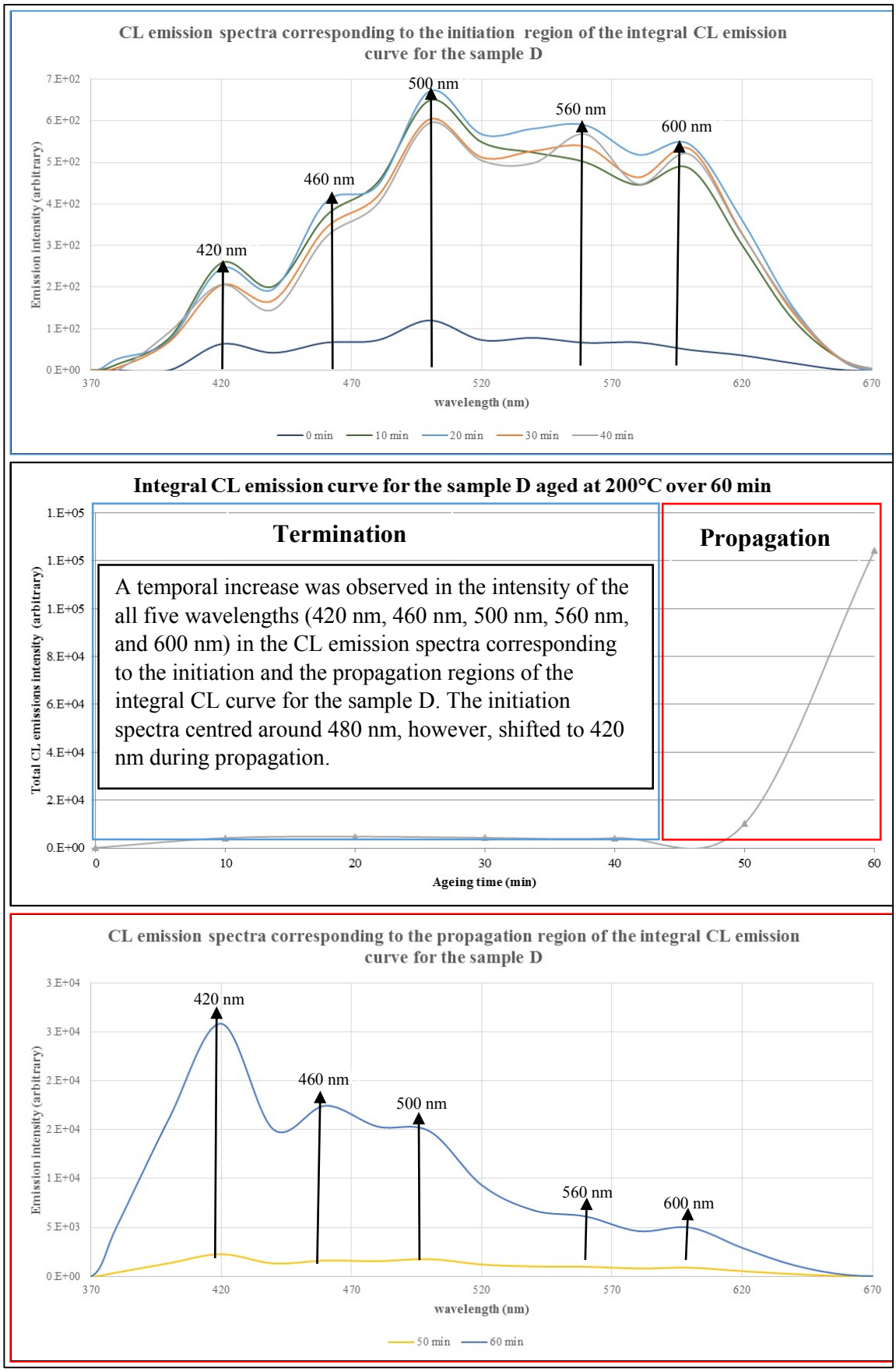


Figure: 5.9. Integral CL curves and corresponding emission spectra for the formulation D.

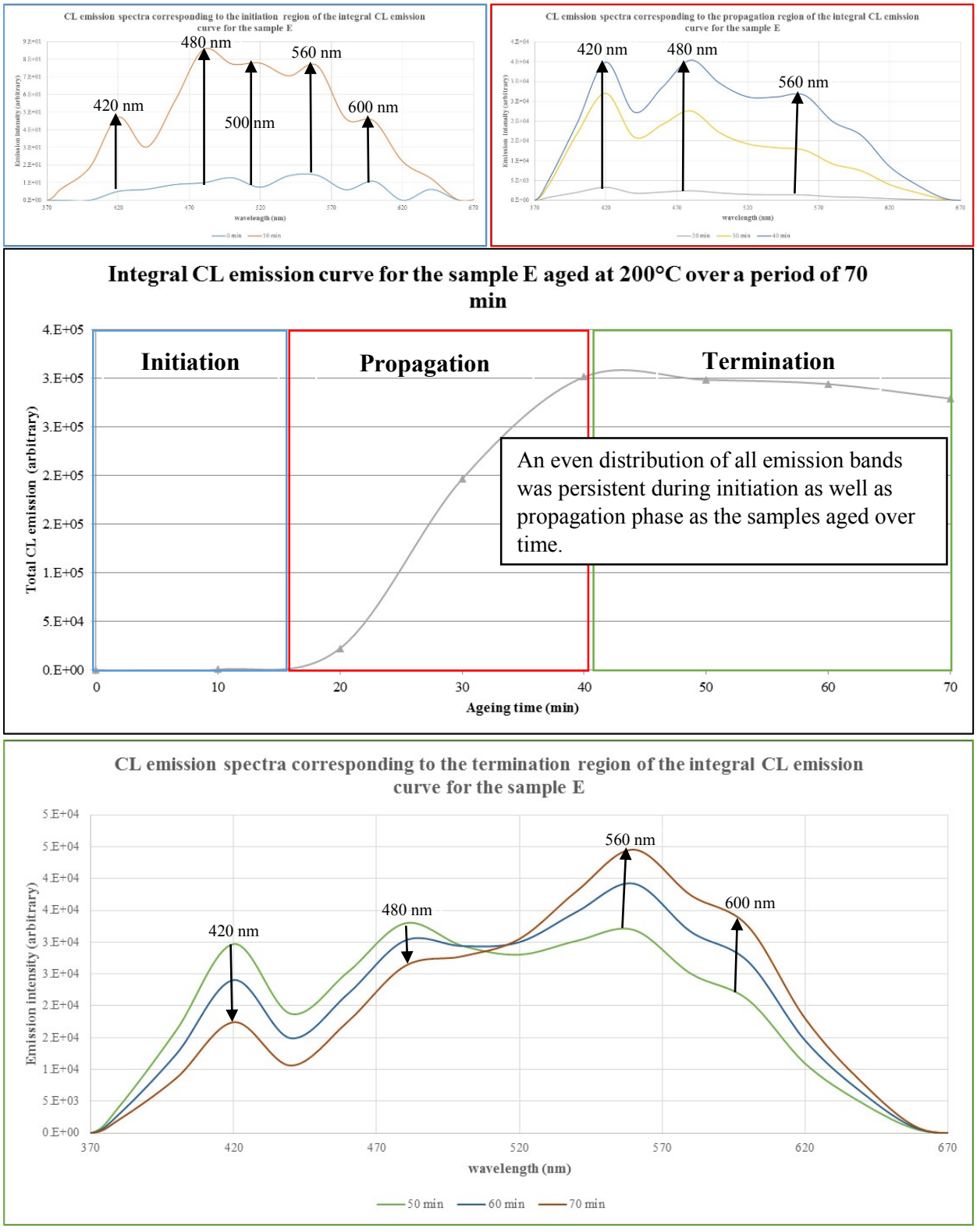


Figure: 5.10. Integral CL curves and corresponding emission spectra for the formulation E.

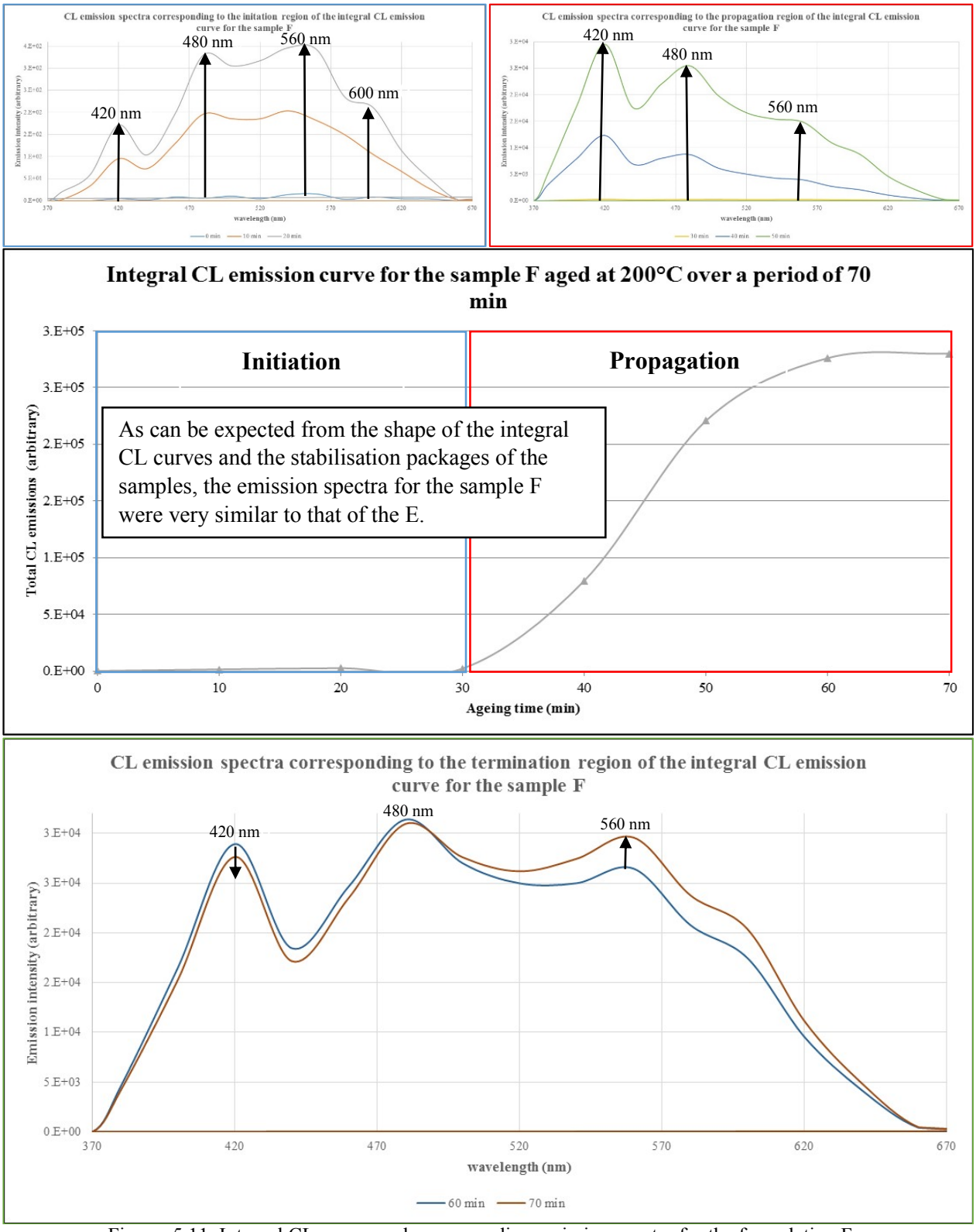


Figure: 5.11. Integral CL curves and corresponding emission spectra for the formulation F.

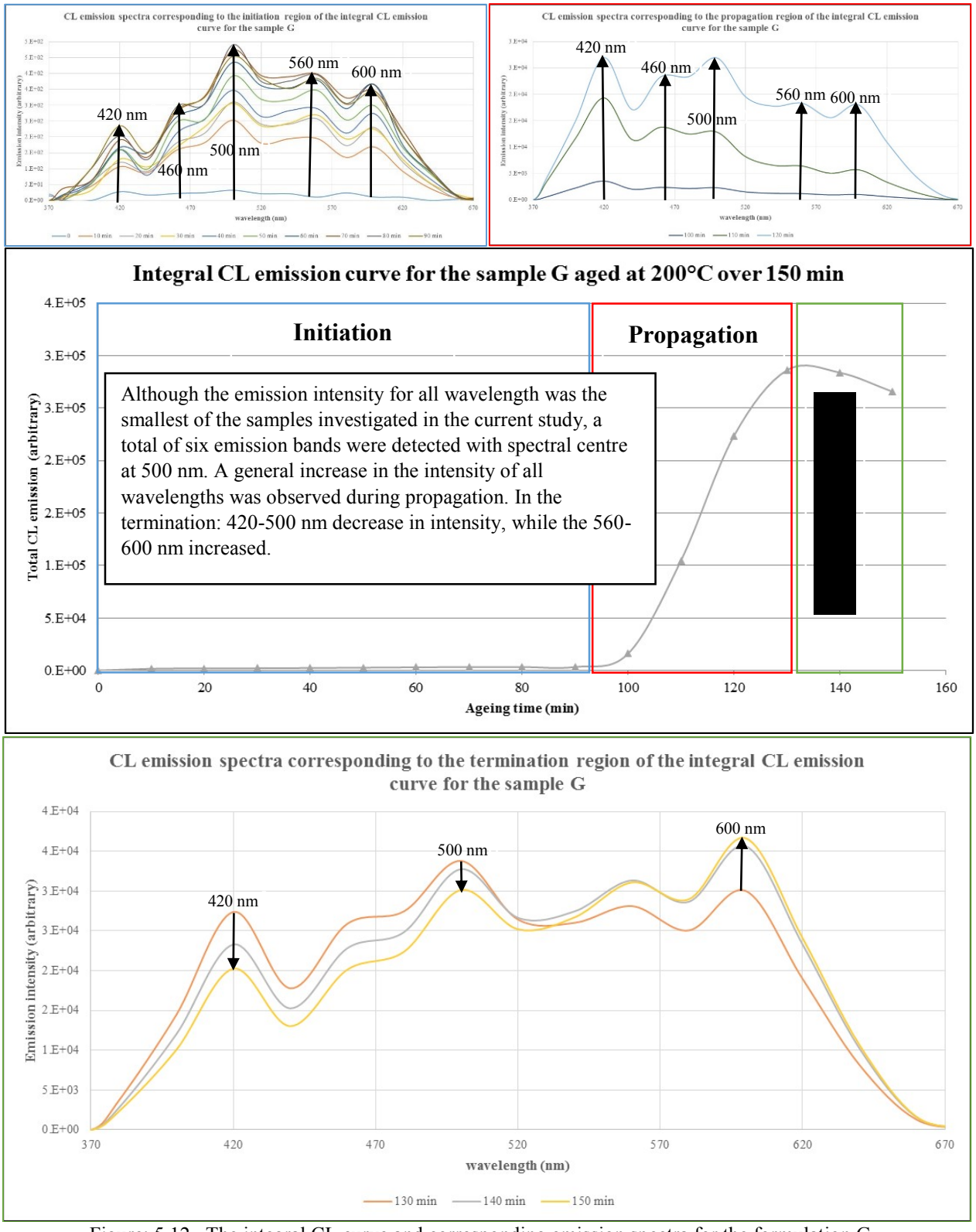


Figure: 5.12. The integral CL curve and corresponding emission spectra for the formulation G.

The CL spectra of the Group: 2 formulations (Table: 2.4) are reported in the Figure: The key feature of the Group: 2 formulations that distinguishes them from the Group: 1 is the replacement of the SN1680 by FS042. The effect of this change on the integral CL intensity has already been reviewed in the previous section. The CL spectra for the formulations are reported in the Figure: 5.13-5.17. A decrease in the number of emission bands was observed in general across the spectra of all formulations; the higher end peaks i.e. 560-600 nm significantly reduced in their intensity. Difference in the intensities of the 420 nm with the other peaks, during propagation phase, was comparatively less pronounced. Addition of thioesters lead to increase in the number of the emission bands. The additional bands thus generated can be due to the stabiliser based species or additional species generated due to the reactions routes triggered by the presence of the thioesters.

Of all the formulation the emission spectrum of the formulation O (5.20) was the most peculiar, as could be expected from the peculiar composition of its stabilisation package i.e. SL1190 was only present in this formulation. The nature and relative concentration of the CL-emissions was more dynamic than any other formulation, propagation phase was characterised by all five bands with a more even distribution of their intensities. Finally, the termination stage did not have the typical pattern of simultaneously increasing and decreasing intensity regions as observed for the rest of the formulations, instead a regular decrease for all peaks of the spectra was observed.

Simple inferences that can be made at this point are: multiple carbonyl species are present in a polymeric sample right from the inception of the ageing period, overtime not only the intensity but also the relative distribution of the individual species varies. The carbonyl species characteristic of 420 nm emission increase more than the other species during propagation, in general. Toward the termination phase a simultaneous increase in the upper half of the spectrum i.e. 500-600 nm, and a decrease in the lower half of the spectrum i.e. 420-500 nm, is another typical feature of CL emission spectra of stabilised PP formulations.

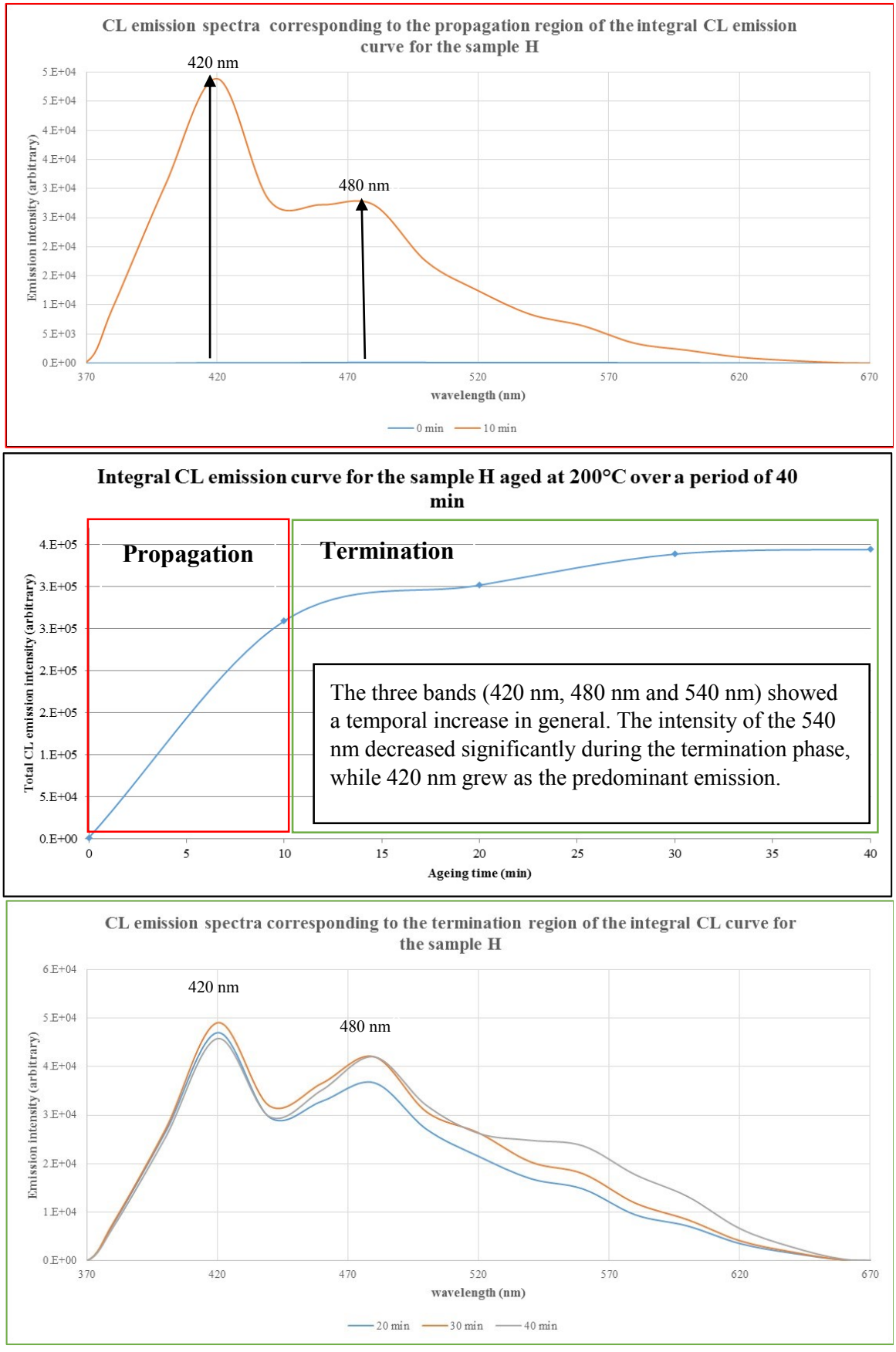
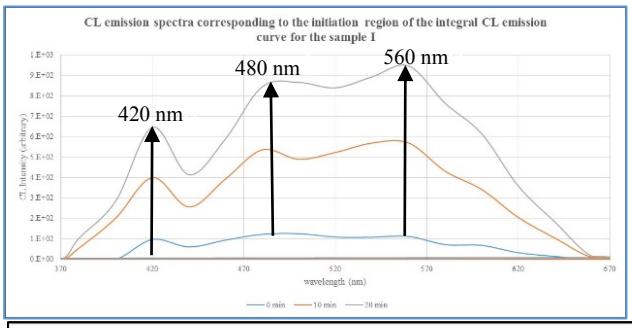
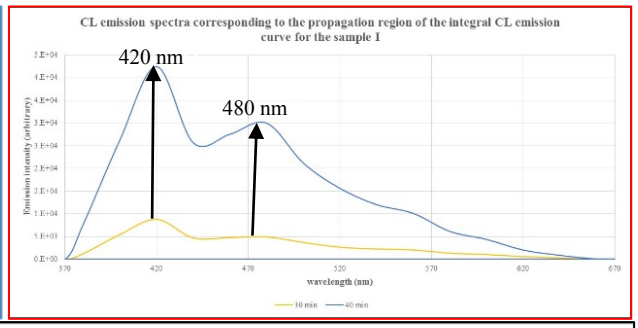
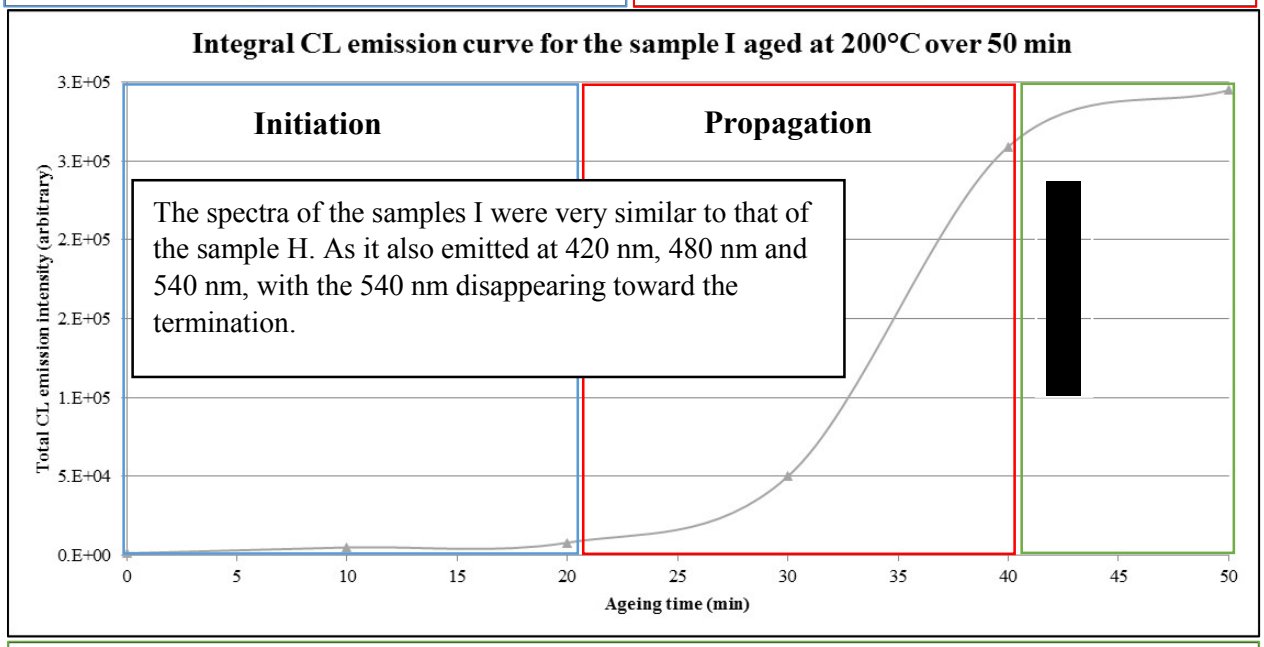


Figure: 5.13. Integral CL curves and corresponding emission spectra for the formulation H.







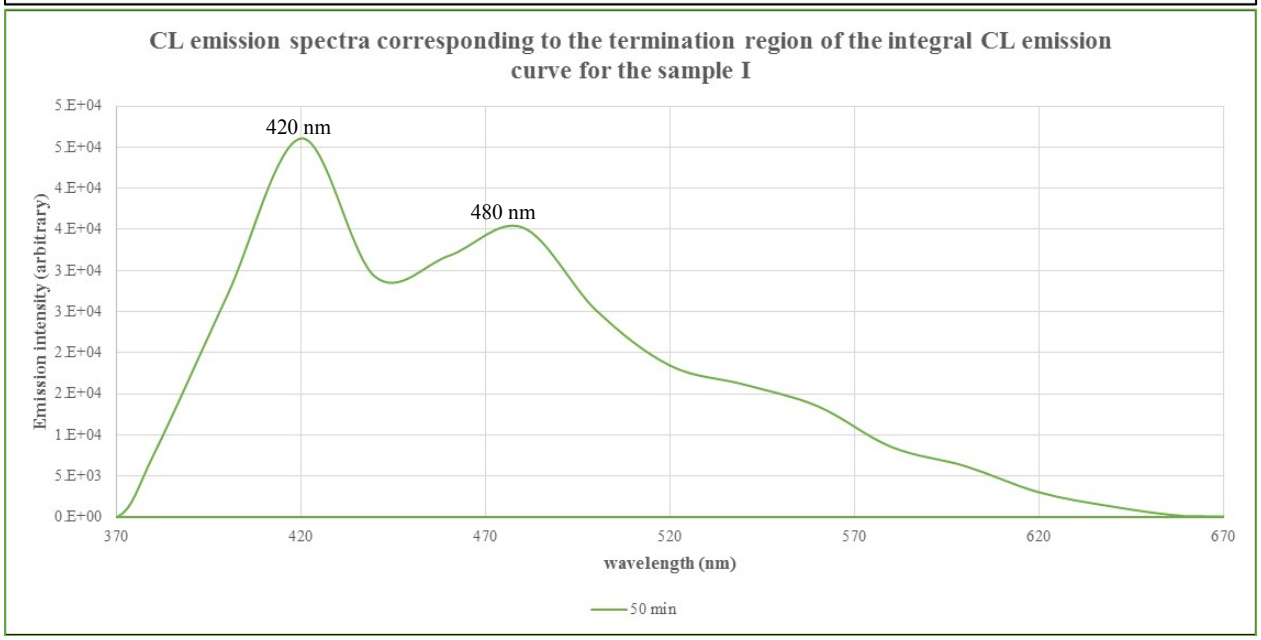


Figure: 5.14. Integral CL curves and corresponding emission spectra for the formulation I.

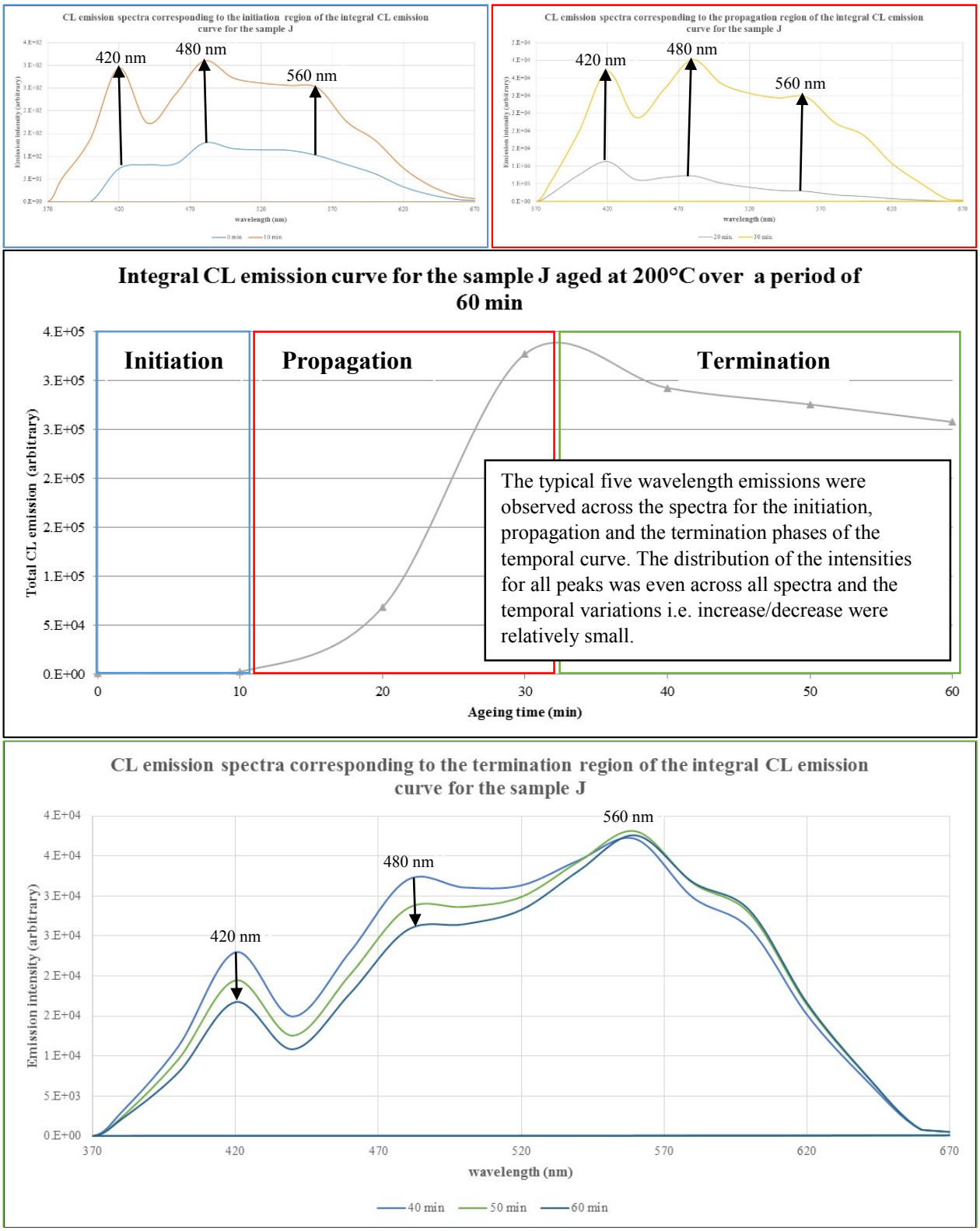


Figure: 5.15. The integral CL curve and corresponding emission spectra for the formulation J.

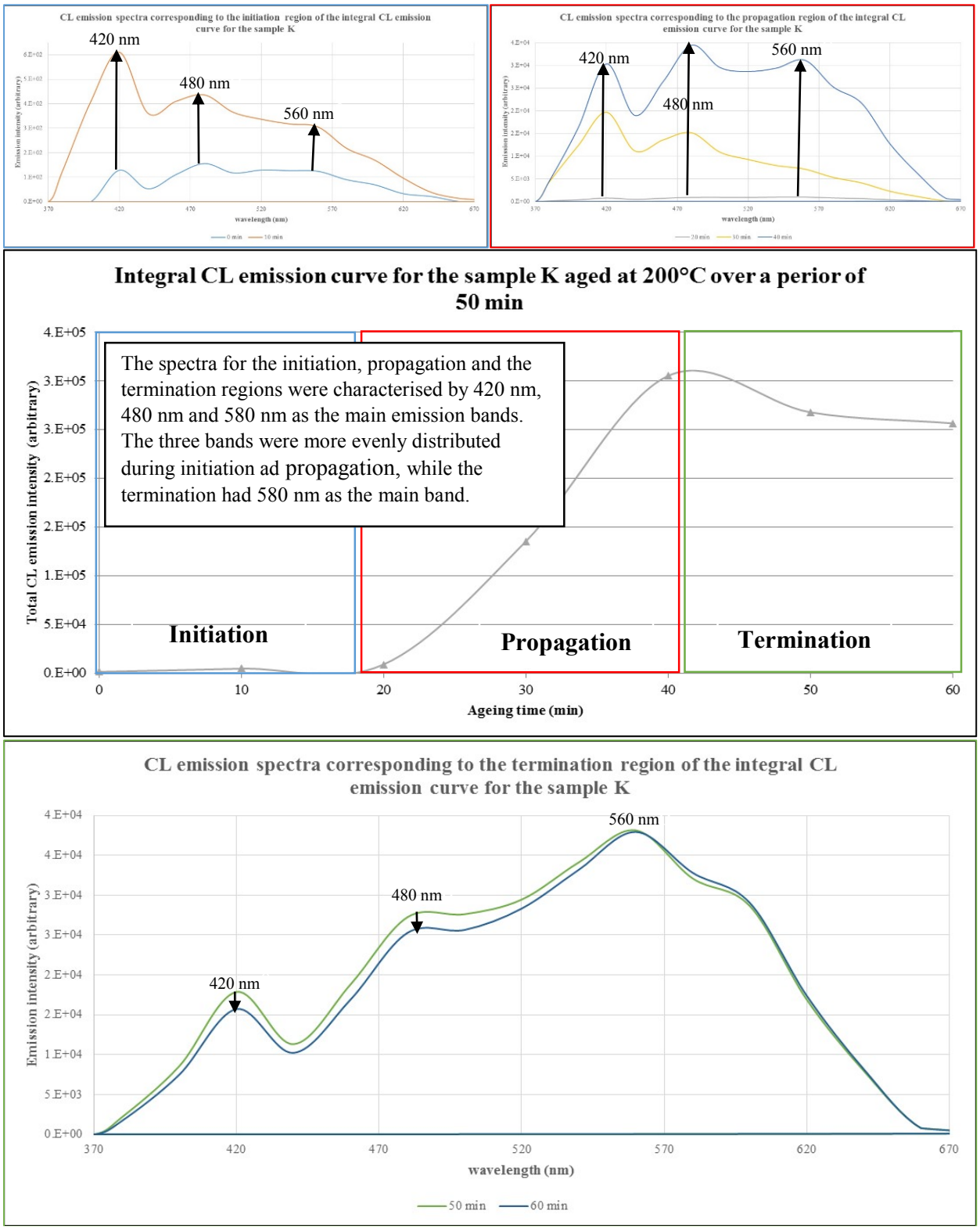


Figure: 5.16. The integral CL curve and corresponding emission spectra for the formulation K.

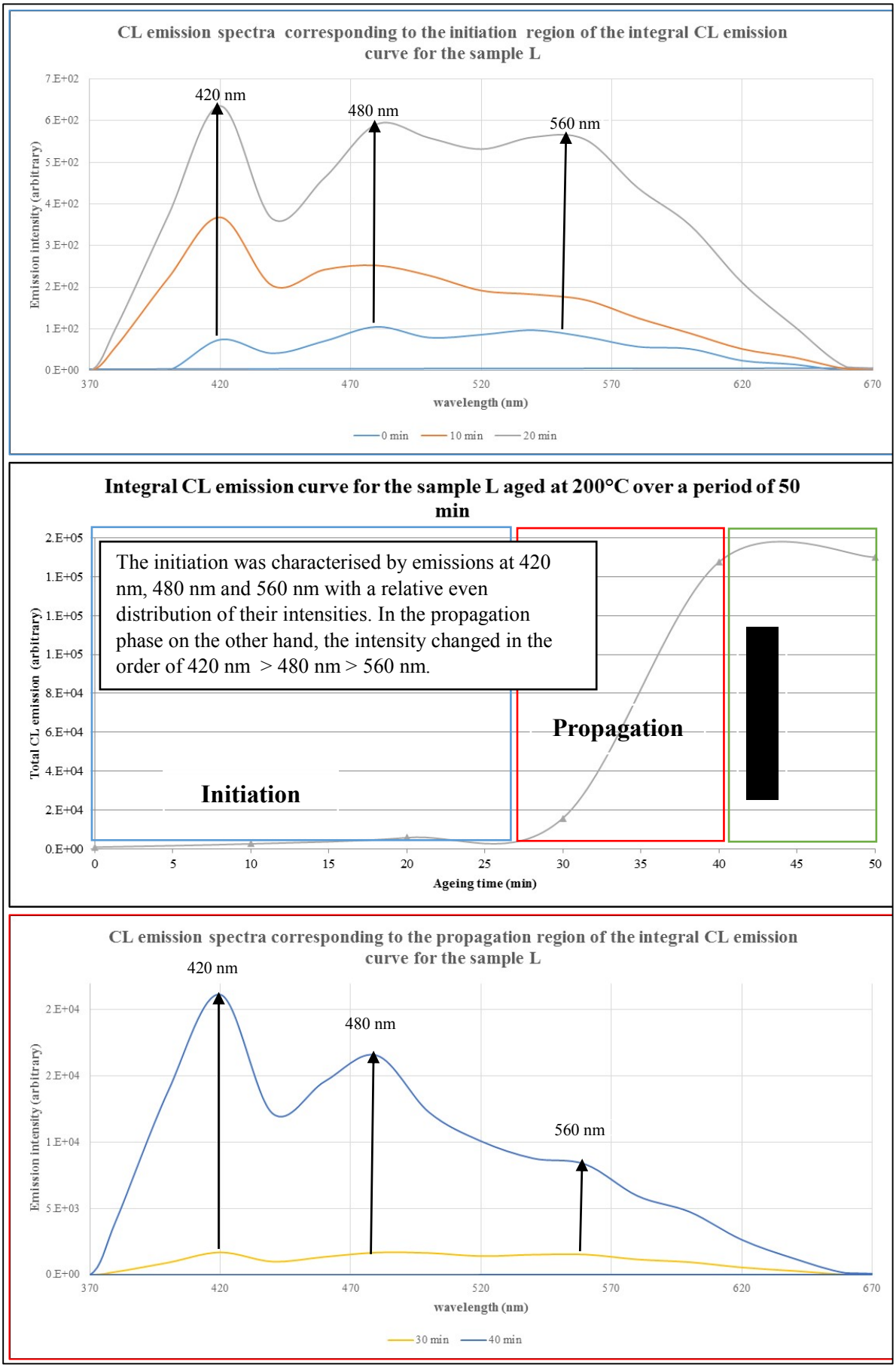


Figure: 5.17. Integral CL curves and corresponding emission spectra for the formulation L.

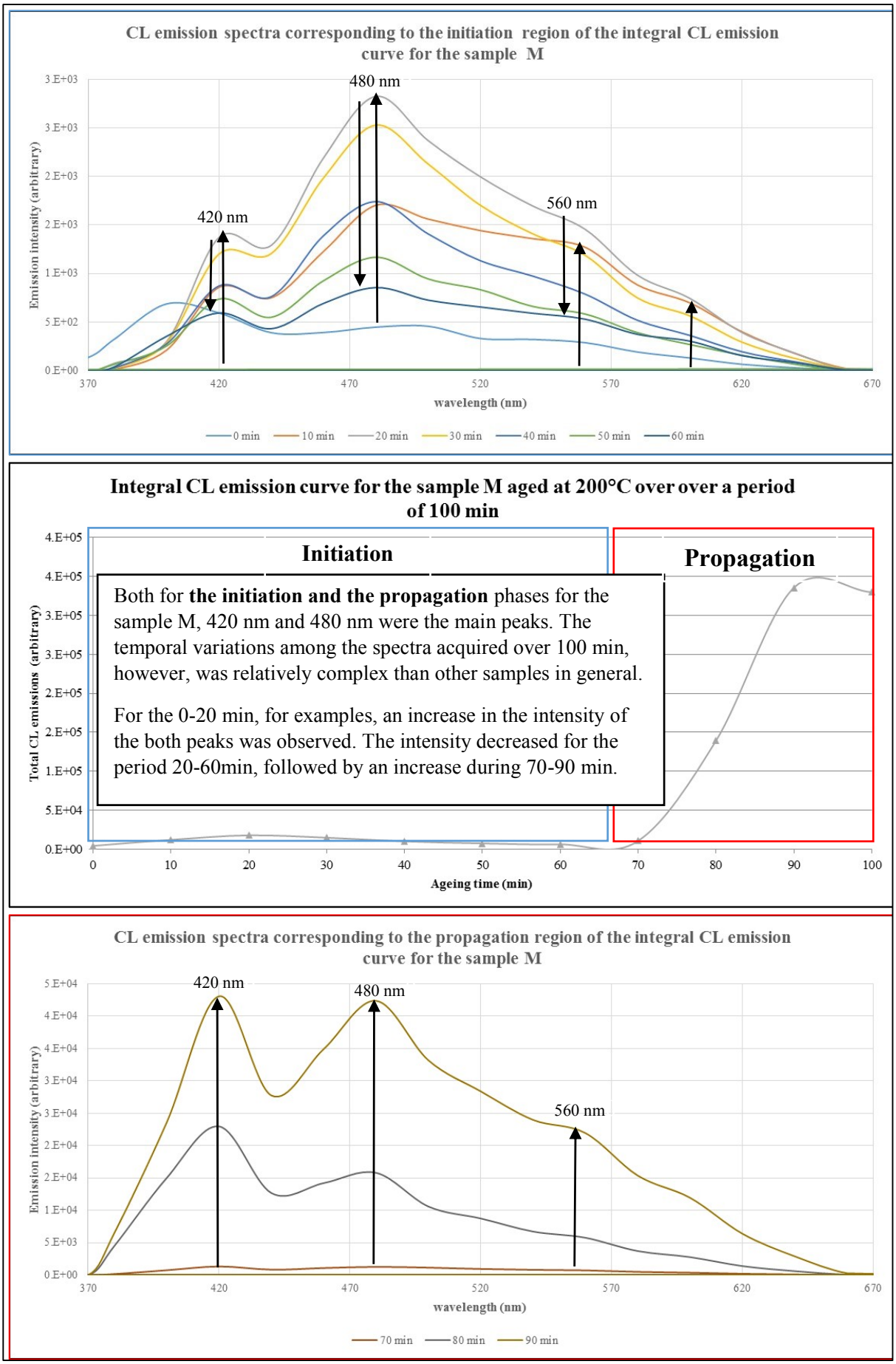


Figure: 5.18. Integral CL curves and corresponding emission spectra for the formulation M.

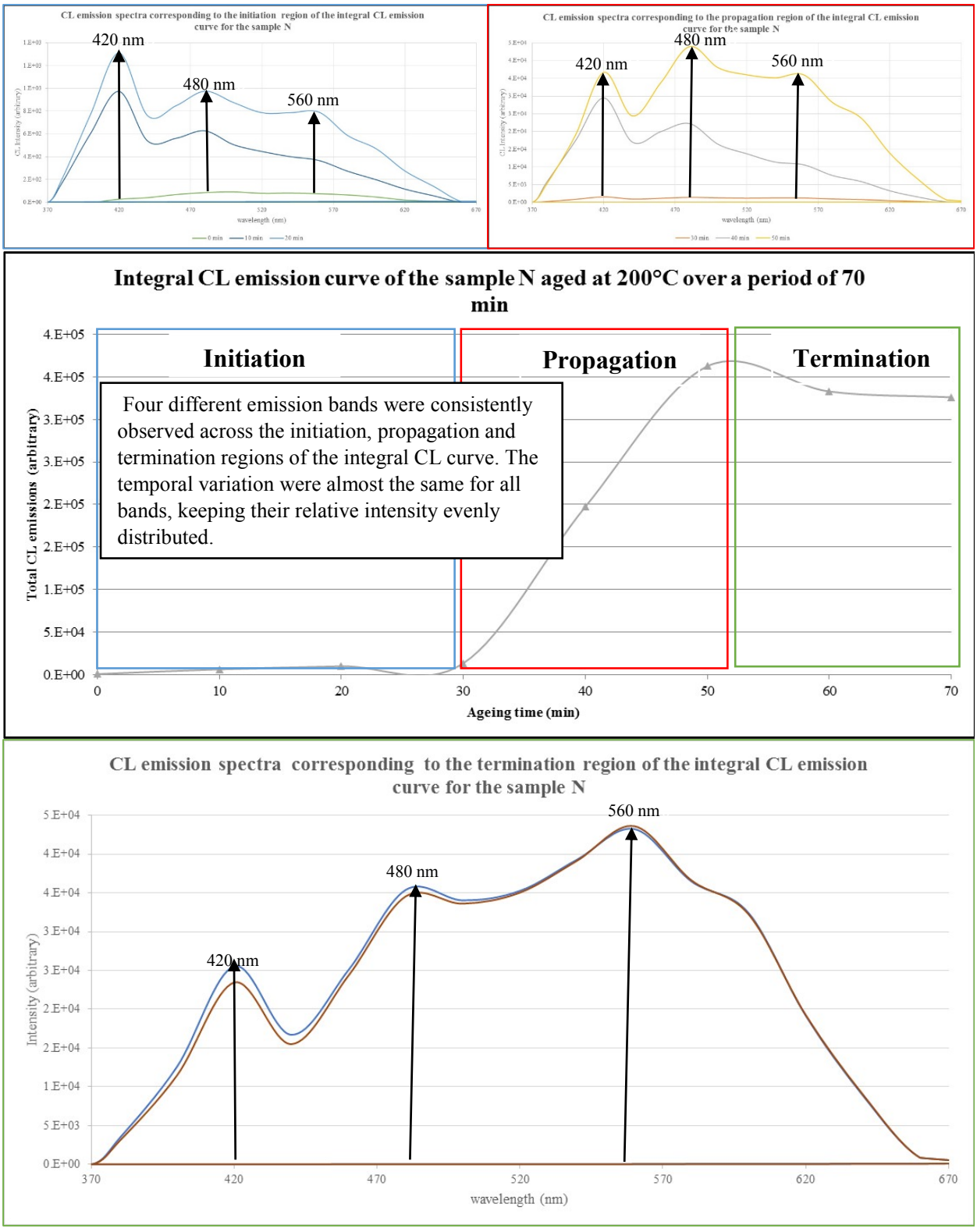


Figure: 5.19. Integral CL curves and corresponding emission spectra for the formulation N.

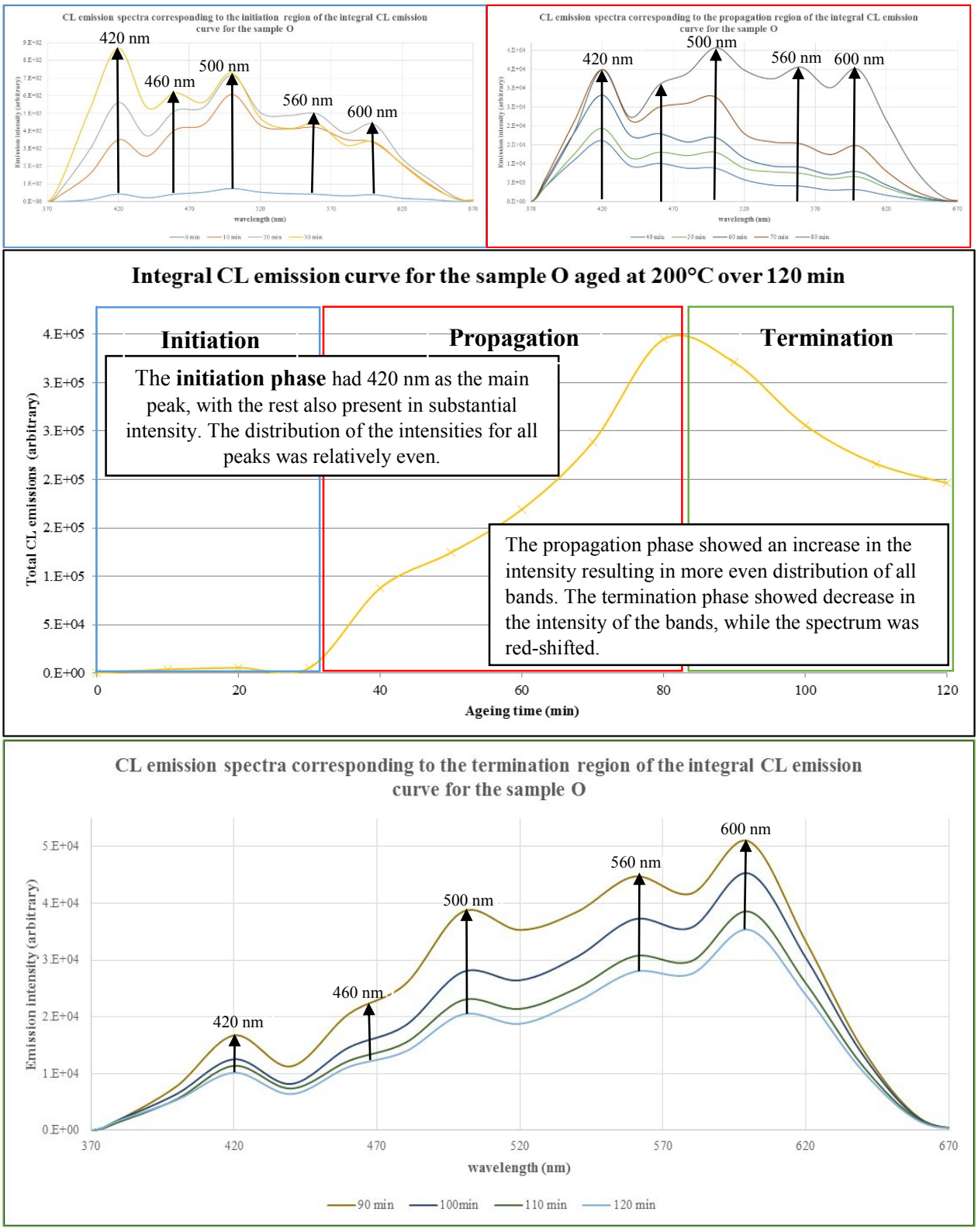


Figure: 5.20. The integral CL curve and corresponding emission spectra for the formulation O.

CHAPTER: 6. EMISSIONS FROM POLYPROPYLENE

6.1. Analysis of PP emissions

Both the IR and CL spectroscopic analysis of the stabilised PP formulations revealed different aspects of thermo-oxidative degradation in the polymer. The IR spectra, for example, demonstrated key variations in the type of the oxidation products generated inside the polymeric matrix as it went through 20 hrs of oxidation at 150°C, 120°C and 90°C. The relatively less obvious chemical changes became more evident at 150°C. The observations also showed that thermo-oxidative degradation in PP is significantly affected by the stabilisation packages used in the polymer. The initial IR spectroscopic analysis hence, provided useful grounds to extend the experimental work further, to study the degradation in molten-state (CL analysis) and headspace of the polymer (Chromatographic analysis). Due to higher sensitivity of the technique and physical state of the samples i.e. molten mass, the CL analysis generated better-defined patterns, especially in the form of integral CL intensity. Differences in the degradation and stabilisation behaviour of the formulations as well as interactions among the antioxidants of various families were evident. Further, unlike the IR spectra, the CL emissions spectra contained a larger number of CL bands, demonstrating the presence of a more diverse and heterogeneous group of oxidation species. The chemical nature of the species, however, could not be ascertained at this stage. The next experimental strategy was the analysis of the emissions made by the PP samples during their thermo-oxidative degradation. Such an analysis was expected to allow identification well as quantification of the chemical species that are generated during thermo-oxidative degradation. The emissions could be used as an indirect way to understand the prevalent degradation chemistry inside the solid polymeric mass.

The emissions in the current study were analysed by SPME-GC-MS and MSSV-GC-MS methods. The two methods were adopted after an initial method development work explained in details in the Chapter: 3 of this report. The compounds detected among the emissions were also semi-quantified, and are reported as percent total emissions in the current section (Table: 6.1-6.15). Use of two different methods i.e. SPME-GC-MS and MSSV-GC-MS, added additional method validation aspect to the work, the methods however, varied in basic experimental conditions significantly. Such difference need to be taken into consideration in any discussion involving a comparison of the results acquired by the two methods (Chapter: 6 and Chapter: 8). The Section: 6.1.2 of the current chapter of this report elaborates on this aspect. The MSSV-GC-MS data, in the current report, is only included for the purpose of its comparison with

SPME-GC-MS, and to demonstrate the former as a useful analytical technique to analyse emissions from polyolefin.

The content of the current chapter mainly comprises of emission profiles of the stabilised PP formulations (Table: 2.3-2.5) acquired by SPME-GC-MS method. The key trends in the qualitative and quantitative aspects of the emissions are reported along with a detailed discussion on the effect of thermal and temporal conditions, as well as the effect of the stabilisation packages used in the formations. The results are subsequently reviewed in the context of the established mechanisms and kinetic models of PP degradation (Section: 6.1.1.2.5). Unlike majority of the studies on PP emissions, the current study consider both the polymer and any incorporated additives for their contribution to the emissions (Section: 6.1.1 and Section 6.1.3). The stabilisation behaviour of the individual antioxidants as well as their mutual interactions are attempted to be explained using the emissions data in corroboration with the spectroscopic results (Section: 6.1.3).

For convenience in interpretation and discussion of the results, the emissions from the fifteen formulations analysed in the current study, are discussed as three sub-groups (6.1.1.2.1, 6.1.1.2.2, and 6.1.1.2.3), which for the sake of reminder for the reader are described below:

- The Group: 1, as shown in the Table: 2.3, comprised of seven different P formulations. The samples donated by A-G, contained two different hindered phenols (SN1010 and GA-80) and two thioesters mixed in six different combinations. All formulations had SN1680, a phosphite as the processing stabiliser in them. A formulations containgin only SN1680 was prepared to serve the blank for the other formulations. CaSt was another common components of all samples in the Group: 1 formulations.
- As shown in the Table: 2.4 of the Chapter: 2, the Group: 2 of the PP formulations was prepared by replacing by SN1680 in the Group: 1 formulations (Table: 2.3) with FS042, while rest of the components and their percentages were kept unchanged.
- The third group of PP formulations, as shown on the Table: 2.5, comprised of three different PP formulations i.e. the formulation M, N and O. The samples in this group were unique:
  - As the sample M had a natural antioxidant, Vitamin E in it. Vitamin E is not previously tested for its emissions while in a PP matrix.
  - Similarly, in the sample N, the previously used antiacid, CaSt, was replaced with ZnO.

- The formulation O of the Group: 3, was based on a combination of the SN1680 with a UV-stabiliser SL1190.

In addition to the stabilised formulations, the emissions from un-stabilised PP have also been analysed using PP in its extruded powder form. Further, a comprehensive analysis of the emissions from the additives at their own was done under the same experimental conditions as the polymeric formulations containing the same additives (Figure: 6.12-6.15). The analysis of the additives at their own was important: to investigation degradation behaviour of the additives and the effect of the polymeric matrix and other stabilisers on it. It also helped in identification of the antioxidant-based degradation products detected in the headspace of the PP formulations containing the same additives as a part of their stabilisation packages. The degradation of the additives also reflected thermal stability of the additives, which is an important feature potentially, affecting the stabilisation capacity of an antioxidant.

6.1.1. Analysis of the emissions by SPME-GC-MS

SPME-GC-MS analysis of emissions from PP and the PP based formulations was done for degradation of the samples at 90°C, 120°C and 150°C for a total period of 20 hrs. During the 20 hrs of ageing the SPME fibre that was exposed to the headspace of the polymer was intermittently desorbed for the intervals: 0-2 hrs, 2-8 hrs and 8-20 hrs, thus generating a temporal profile of emissions from the formulations, for the respective degradation periods. The compounds identified in the headspace of the PP formulations were also semi-quantified. The quantification was done by automated integration of the peak areas on a total ion chromatogram (Section: 2.3.4 and 3.3.4).

6.1.1.1. Identification of the emissions

A large number of compounds belonging to a wide range of functionalities were detected in the headspace of the PP formulations as the samples were aged. Conventional methods of identification of the unknowns, by comparing the spectra with appropriate reference material, could have been tricky and costly for the current study mainly due to the large number of the compounds that required to be identified. The identification therefore, was conducted based on:

- Molecular ion identification in the mass spectra

- Fragmentation patterns and base-peaks, characteristic of various functional groups i.e. m/z: 58, 60 and 82 as base peaks in the spectra of ketones, acids and aldehydes.
- Relative peak position i.e. peak retention time, e.g. acids are eluted after aldehydes and ketones, and peak shapes, e.g. carbonyls have broader peaks due to their higher reactivity for a GC column.
- Comparison of the mass spectra with the MS databases i.e. NIST and WILEY online MS libraries, and relevant published literature (Figure: 3.18-3.21) [60, 108].

Following this approach majority of the compounds in PP emissions were successfully identified. Un-identified compounds are marked with '?' in the data tables throughout the current chapter, and does not form a significantly large proportion of the results. Further, provided that a large number of the compounds, especially hydrocarbons and antioxidant fragments, were repeatedly observed among the emissions, the identification process gained an edge (Figure: 6.1 and 6.4).

As shown in the Table: 6.1-6.15, choice of a sensitive analytical method, range of ageing conditions, and the diverse selection of the stabilisation packages in the PP-formulations led to highly comprehensive overview of the emissions from PP. The wide range of the data had to be boiled down to key groups for ease in interpretation and subsequent discussions. In the results, there were compounds and functionalities repeatedly reported, and those which have not been reported/detected previously, e.g. degradation products of the antioxidants etc.

In general, a range of hydrocarbons i.e. alkanes and alkenes with the later forming only a minor proportion, carbonyls and aromatics were detected among the emissions (Figure: 6.8 and Table: 6.1-6.15). The hydrocarbons were mainly in the range of C3-C24 compounds with extensive isomerism for almost every molecular mass detected (Figure: 6.1 and 6.4). Accurate assignment of the individual hydrocarbons was hindered by the limitations of the available instrumentation. Throughout the current study, therefore, all isomers corresponding to a particular mass are reported as a single compounds i.e. all hydrocarbons with the mass of 170 Da are denoted as dodecane (Figure: 6.1 and Table: 6.1-6.15). As evident from the data sets given in the Table: 6.1-6.15, a clear pattern indicating chain scission at every third carbon of a PP chain has been observed among the hydrocarbon emissions. As far as the mechanistic explanations and

implications of the hydrocarbon-based emissions for thermo-oxidative degradation of PP are concerned, it has previously not been discussed in breadth. Due to comparatively less toxic effects and their omnipresence, indeed, the hydrocarbons have mainly been ignored in most of the discussions on PP emissions. The current study reveals that a more detailed analysis of the hydrocarbon-based emissions, especially accurate identification of the isomers, can provide a good insight into the chain scission patterns in PP. Another aspect that makes hydrocarbons important is their early presence among the emissions i.e. generated as early as during first few minutes of thermo-oxidative degradation and at a temperature as low as 90°C (Table: 8.1-8.2).

Carbonyls, the second major group of PP emissions, are a more direct indication of polymer oxidation. Their presence has been found negligible at low degradation temperature i.e. 90°C and 120°C, in most of the formulations (Figure: 6.3 and Table: 6.1-6.3 and Figure: 6.4-6.6). However, a significantly higher emission of the carbonyls was observed for degradation at 150°C (Figure: 6.3 and Table: 6.9-6.15). The carbonyls detected at 150°C contained features that were unique to each of the formulations (Figure: 6.7). A mixture of ketones, aldehydes, acids, esters and alcohols in general, became predominated by aldehydes for the formulations E and F and those containing hydroxylamine as the processing stabilisers. Similarly, the presence of phosphite (SN1680) in combination with the hindered phenols and thioesters, exhibited comparatively higher ketone emissions than the formulations that contained a hydroxylamine (FS042). The variation in the relative proportion of each of the carbonyl groups was significant across the formulations, and changed with ageing time and temperature (Figure: 6.6-6.7 and Table: 6.1-6.15). Another key difference between the formulations containing SN1680 and FS042, was the higher proportion of hydrocarbons emissions in the former.

6.1.1.2. Quantification of the emissions

The peaks successfully identified as emissions from the PP samples analysed in the current study, were quantified by automated integration of the peak areas (Section: 2.3.4 and 3.3.4, and Figure: 3.26). The data corresponding to the major groups as well the individual compounds detected in the headspace of the aged samples is reported in the Table: 6.1-6.15. The semi-quantitative data thus obtained demonstrated thermal and temporal variations as well as the effect of stabilisation packages (Figure: 6.2) on the quantitative and qualitative aspects of the emissions. In the emissions data thus obtained, there are features that are common across the samples, those unique to the individual sample. Variations were observed at the level of total

emissions, emission groups as well as individual compounds (Figure: 6.2 and Figure: 6.6-6.7). Such differences among the formulations were discernible as early as during the first 2 hrs of polymer ageing, becoming only more pronounced and reflective of the role of the stabilisation packages over prolonged ageing and at higher temperature. As can be seen in the Figure: 6.2, while the high emitting formulations i.e. H, I, J and K, consistently remained the high emitting, total emissions from the lower emitting formulations i.e. B, C, D, M and N, reduced further overtime. At 90°C, all formulations demonstrated an increase in the total emissions. At 120°C and 150°C, on the other-hand, the behaviour was more complex. At 120°C, for example, a temporal decrease was observed in the total emissions from the Group: 1 formulations (Table: 2.3), while a temporal increase was demonstrated by the rest of the samples i.e. the Group: 2 and the Group: 3 samples.

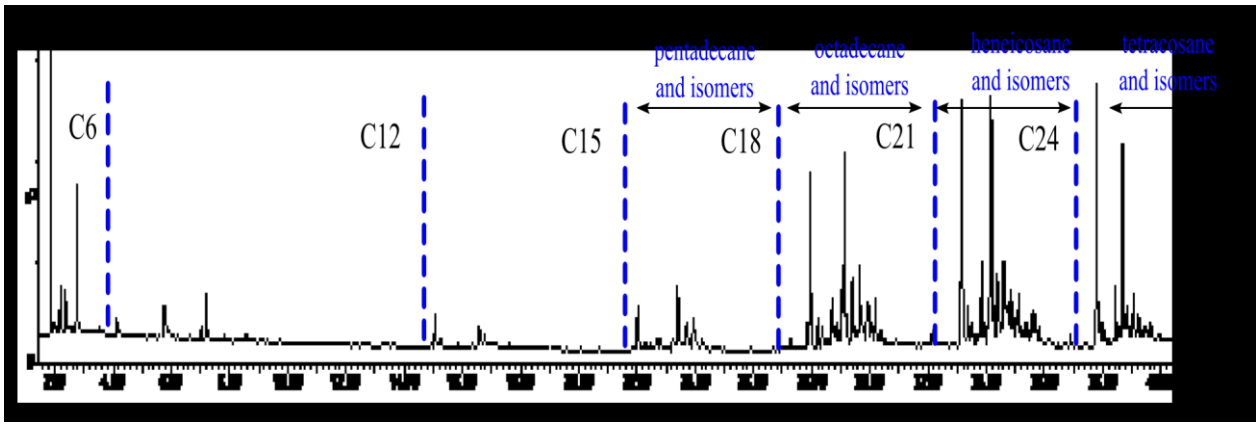


Figure: 6.1. Typical hydrocarbon emissions generated by degradation of stabilised PP.

The inter-sample variations of among total emissions data became more pronounced for degradation at 150°C. At 150°C, the formulation A was identified as the least stable, while the formulations G showed highest stability and very low emissions. Further, at 90°C the total emissions increased consistently across the formulations, following a linear or a second polynomial order. At 120°C and 150°C, the changes in the total emissions among the formulations were more diverse. At 150°C, for example, a temporal decrease of linear and second order polynomial was observed for most of the formulations, except for the formulations A, H, and L-M, which showed a temporal increase instead. The emissions at 150°C demonstrated a stronger correlation with the CL data for the corresponding formulations. The formulation A and H, for example, have been observed to be the least stable by both techniques. Unlike 90°C and 150°C, the temporal changes in the total emissions at 120°C, were less abrupt than the other two ageing temperatures.

As reported in the Section: 6.1.1, the emissions from the PP formulations comprised of multiple functionalities. Relative proportion of the various groups and the individual compounds varied across as well as within the formulations in response to ageing conditions i.e. temperature, time, oxygen availability, and composition of the stabilisation packages in the PP formulations. Any such variations can be linked to the chemistry in-operation in the PP matrix of a given PP formulation. It is this aspect, along with detailed overview of the corresponding emissions data, focused in the discussion in the current chapter.

6.1.1.2.1. Hindered phenols, thioester and phosphite based formulations

Thioesters and hindered phenols are two important groups of antioxidants used for PP stabilisation in commercial applications of the polymer. The antioxidants from the two groups are known for a mutual synergy and therefore, are used together for PP stabilisation. Further, the hindered phenols have an additional edge as stabilisers due to their positive impact on the stabilisation generated by the phosphite-type antioxidants (SN1680 in the current study). The poor stabilisation attained by SN1680 only, e.g. in the formulation A (Figure: 6.5), has been observed to increase in presence of a hindered phenols significantly, e.g. the formulation B and C (Figure: 6.3). The increase in the stabilisation capacity of SN1680 in presence of SN1010 has been reported due to controlled consumption of the phosphite in the presence of hindered phenols [27]. For the current study, two hindered phenols i.e. SN1010 and GA-80, and two thioesters i.e. DSTDP and SN4120, were concocted along with the SN1680 to get seven different stabilisation packages (Table: 2.3). Expecting that the variations in the stabilisation packages does get reflected in the degradations products generated by the polymeric matrix and by the antioxidants themselves, the emissions from the Group: 1 formulations are overviewed in the current section.

The stabilisation packages that define the Group: 1 formulations (Table: 2.3), with the exception of the formulation A, are meant to provide adequate stabilisation in PP for commercial application.

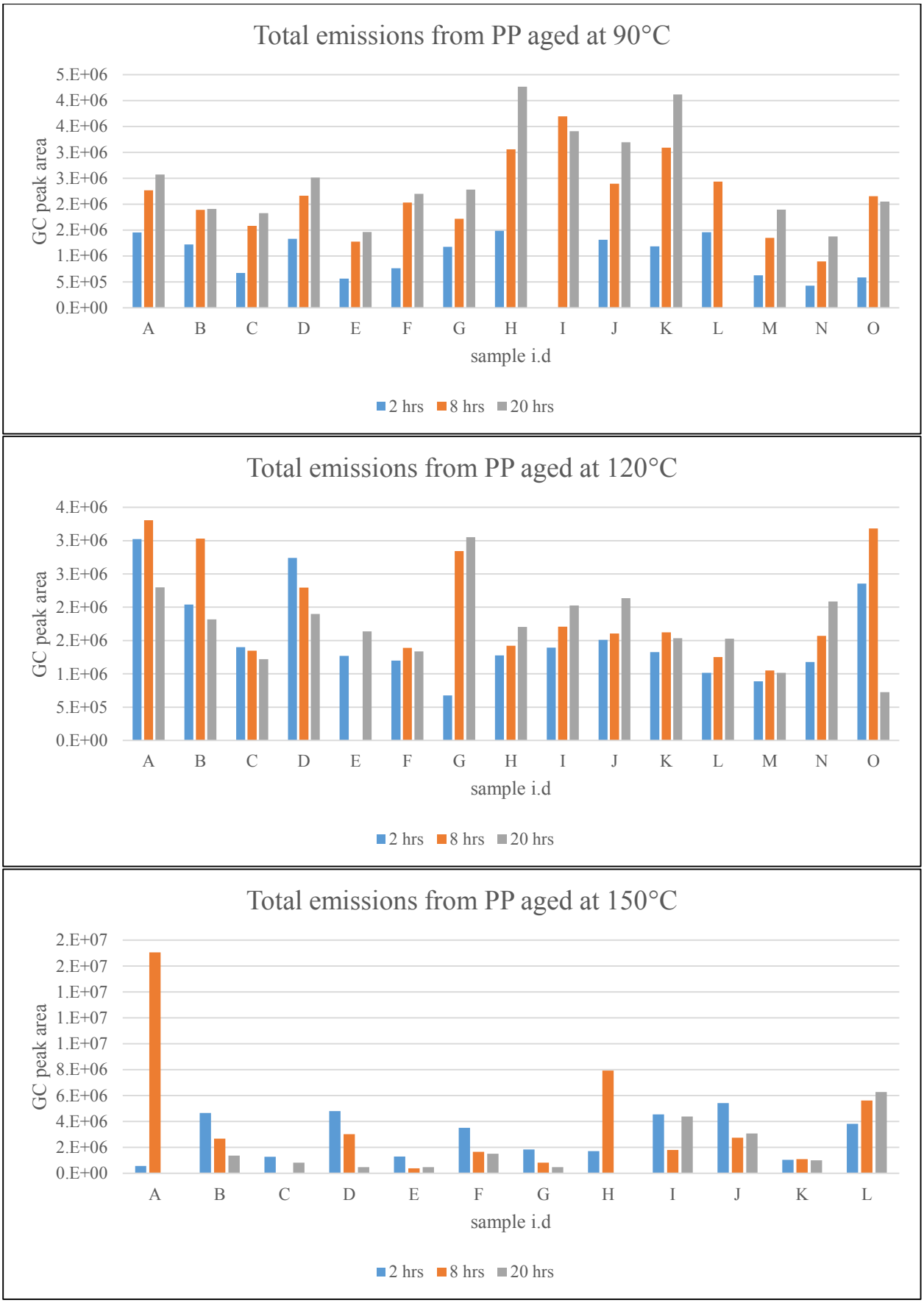


Figure: 6.2. Thermal variation in the total emissions for the formulation. (*The data for the sample L for the 90°C emissions is missing due to instrument failure and corruption of the software used for data processing*).

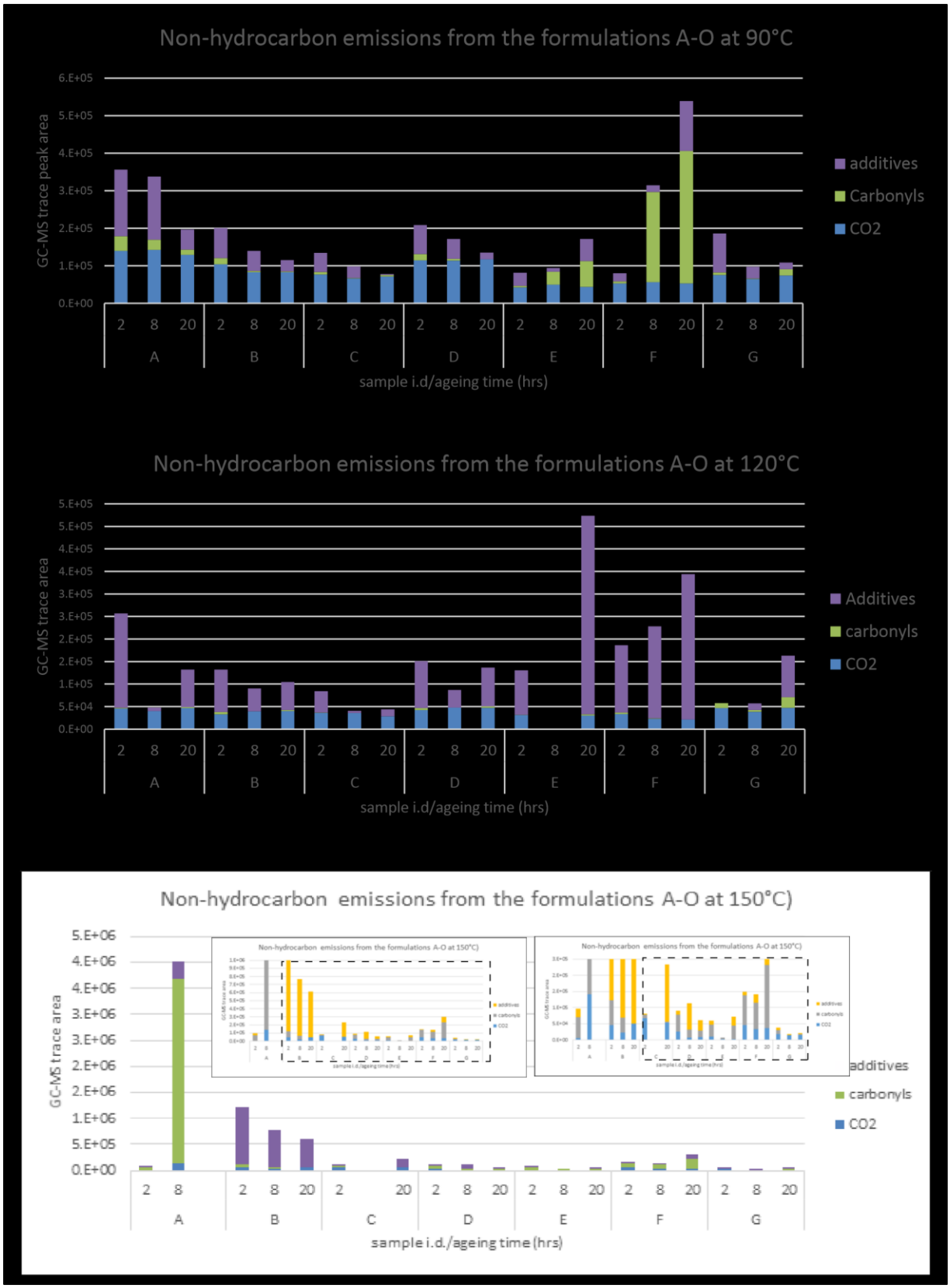


Figure: 6.3. Key groups of non-hydrocarbon emissions from the formulations A-G.

In all formulations, however, significant emissions were observed for ageing at 90°C, 120°C and 150°C. Irrespective of the ageing conditions and the composition of the stabilisation packages, hydrocarbons formed the major part of emissions i.e. 70-90% (Table: 6.1-6.15), in all samples of the Group:1. The hydrocarbons were mainly alkanes in the range of C3-C27. Increase in ageing temperature and time led to increase in the size of the alkanes detected among the emissions (Figure: 6.4). At 90°C, for example, C12 and C15 were formed as the major part of hydrocarbons i.e. 60-70%, which was shifted to C15 and C18 within next six hours of ageing. Although the alkenes formed only a minor portion of the total hydrocarbon emissions, the relative proportion did change for some formulations, e.g. the formulation C, for example, generated relatively higher unsaturated hydrocarbons across the range of ageing temperatures i.e. 90°C, 120°C and 150°C. As far as the carbonyls are concerned, no alcohols, esters and acids were detected in any of the Group: 1 formulations at 90°C (Table: 6.1-6.3 and Figure: 6.6).

The carbonyl content at 90°C consisted of acetone, 3-pentene-2-one, and methacrolein only (the formulation E and F being two exceptions), and formed only a concentration < 1% of the total emissions.

Table: 6.1. Emissions from the formulations A-G afte r ageing at 90°C for 2 hrs.

Analytical technique			**SPME-GC-MS**						
Sample i.d.			**A**	**B**	**C**	**D**	**E**	**F**	**G**
Ageing temperature (°C)			**90**						
Ageing time (hrs.)			**2**						
m/z	**Formula**	**Names of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS**						
44	CO_2	Carbon dioxide	9.6	8.6	11.3	8.6	7.5	7	6.4
56	C_4H_8	Isobutylene	0.4	0.5	0.5	0.2	0.4	0.4	0.2
72	C_5H_{12}	Pentane	0.5	0.1	0.1	0.1	0.1	0.2	0.1
86	C_6H_{14}	Hexane and isomers	2.1	3.1	4.5	2.5	4.0	3.4	2.4
100	C_7H_{16}	Heptane and isomers	0.1	0.2		0.2			0.2
114	C_8H_{18}	Octane and isomers	1.5	0.4	0.2	0.4	0.5	0.1	0.3
112	C_8H_{16}	Octene	0.6	1.2	0.4	1.3	0.2	0.2	1.2
128	C_9H_{20}	Nonane and isomers	8.1	7.8	5.1	7.6	5.9	4.7	7.3
142	$C_{10}H_{22}$	Decane and isomers	0.4	0.4	0.1	0.5	0.7		
156	$C_{11}H_{24}$	Undecane and isomers	2.0	0.4	0.5	0.5	0.6	0.7	
170	$C_{12}H_{26}$	Dodecane and isomers	22.6	28	20.8	25.7	22.5	22.1	26.3
212	$C_{15}H_{32}$	Pentadecane and isomers	36.4	36.9	42.2	41.4	46	46.3	39.0
254	$C_{18}H_{38}$	Octadecane and isomers		4.2	4.8	3.6	3.3	6.6	6.5
Total percentage of hydrocarbons in the polymer headspace			75.0	83.5	79.3	84.3	84.0	84.5	84.0
94	?	?	0.6	0.2	0.2	0.1		0.2	0.1
58	C_3H_6O	Acetone	0.3						
98	$C_6H_{10}O$	3-Pentene-2-one,4-methyl		0.4		0.2			
Total percentage of ketones in the polymer headspace			0.3	0.4		0.2			
72	C_4H_8O	Tetrahydro, furan	1.5	0.3	0.2	0.5			
96	C_6H_8O	2,4-Dimethylfurane	0.2						
Total percentage of furans in the polymer headspace			2.1	0.3	0.2	0.5			
70	C_4H_6O	Methacrolein	0.5	0.5	0.6	0.5	0.7	0.5	0.4
198	$C_{13}H_{26}O$	Tridecanal						0.5	
212	$C_{14}H_{28}O$	Tetradecanal						0.4	
226	$C_{15}H_{30}O$	Pentadecanal					1.3	4.0	
Total percentage of aldehydes in the polymer headspace							1.3	5.0	
206	$C_{14}H_{22}O$	2,6-bis (1,1-dimethylethyl) phenol		1.0					
Total percentage of additive-based fragments in the polymer headspace				1.0					

Table: 6.2. Emissions from the formulations A-G after ageing at 90°C for 8 hrs.

Analytical technique			**SPME-GC-MS**						
Sample i.d.			**A**	**B**	**C**	**D**	**E**	**F**	**G**
Ageing temperature (°C)			**90**						
Ageing time (hrs.)			**8**						
m/z	**Formula**	**Names of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS**						
44	CO_2	Carbon dioxide	6.3	4.4	4.2	5.3	4.0	2.8	3.7
56	C_4H_8	Isobutylene	0.1	0.1	0.3	0.3	0.2	0.2	0.2
72	C_5H_{12}	Pentane	0.2	0.1	0.1	0.1	0.1	0.1	
86	C_6H_{14}	Hexane and isomers	1.0	0.9	1.2	0.9	1.0	0.6	0.7
112	C_8H_{16}	Octene	0.4	0.7	0.1	0.6	0.2	0.1	0.8
114	C_8H_{18}	Octane	0.8	0.1	0.1	0.1	0.1		0.1
128	C_9H_{20}	Nonane	4.5	3.2	1.8	3.9	2.0	1.0	3.5
156	$C_{11}H_{24}$	Undecane	1.1	0.1	0.2	0.2	0.2		0.1
170	$C_{12}H_{26}$	Dodecane	12.5	13.8	9.5	15.2	9.8	6.8	13.6
212	$C_{15}H_{32}$	Pentadecane	26.5	29	28.4	29.8	27.1	20.8	30
254	$C_{18}H_{38}$	Octadecane	35.2	44.4	42.3	40.8	44.0	42.3	42.7
296	$C_{21}H_{44}$	Heneicosane	2.6		6.4		6.5	11.5	
338	$C_{24}H_{50}$	Tetracosane			3.1		1.0	0.7	1.5
Total percentage of hydrocarbons in the polymer headspace			84.9	92.0	93.6	92.0	92.5	85.0	93.4
58	C_3H_6O	Acetone	0.1					0.3	0.1
98	$C_6H_{10}O$	3-Pentene-2-one, 4-methyl	0.1	0.2	0.1	0.1	0.1	0.1	0.1
Total percentage of ketones in the polymer headspace			0.1	0.2	0.1	0.1	0.1	0.3	0.1
72	C_4H_8O	Tetrahydro, furan	0.7			0.2	0.1		
Total percentage of furans in the polymer headspace			0.7			0.2	0.1		
184	$C_{12}H_{24}O$	Dodecanal						0.7	
198	$C_{13}H_{26}O$	Tridecanal					1.9	0.8	
212	$C_{14}H_{28}O$	Tetradecanal						0.4	
226	$C_{15}H_{30}O$	Pentadecanal						9.0	
240	$C_{16}H_{32}O$	Hexadecanal					0.7	0.4	
254	$C_{17}H_{34}O$	Heptadecanal						0.4	
Total percentage of aldehydes in the sample headspace							2.6	11.7	
78	C_6H_6	Benzene	0.1			0.1			
92	C_7H_8	Toluene	4.4	1.6	1.1	1.7	0.7	*	1.4
106	C_8H_{10}	Xylene	0.2			1.0	0.4	*	1.4
220	$C_{15}H_{24}O$	2,6-Di-tert-butyl, 4-methylphenol		≥0					
220	$C_{14}H_{20}O_2$	2,6-Di-tert-butyl-1, 4-benzoquinone		0.6		0.3			
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol	2.3	0.6		0.2		0.2	
192	$C_{12}H_{16}O_2$	Neopentyl benzoate	0.5					0.3	
208	$C_{12}H_{16}O_3$	2-Allyl-5-ethoxy-4-methoxyphenol						*	
Total percentage of additive-based fragments in the sample headspace			7.5	2.8	1.1	3.3	1.1	0.9	2.8

Table: 6.3. Emissions from the formulations A-G after ageing at 90°C for 20 hrs.

Analytical technique			**SPME-GC-MS**						
Sample i.ds.			**A**	**B**	**C**	**D**	**E**	**F**	**G**
Ageing temperatures (°C)			**90**						
Ageing time (hrs.)			**20**						
m/z	**Formula**	**Names of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS traces**						
44	CO_2	Carbon dioxide	5.0	4.3	3.9	4.7	3.0	2.4	3.2
56	C_4H_8	Isobutylene	0.3	0.1	0.2	0.1	0.1	0.1	0.2
72	C_5H_{12}	Pentane	0.1	0.1	0.2	0.1	0.2	0.1	0.1
86	C_6H_{14}	Hexane and isomers	0.3	1.0	0.3	0.1	1.3		0.2
112	C_8H_{16}	Octene	0.2	0.5	0.1	0.5	0.3	0.2	0.3
114	C_8H_{18}	Octane	1.0	0.1		0.1	0.1		
128	C_9H_{20}	Nonane	2.0	3.2	0.7	1.6	0.4	0.3	1.6
156	$C_{11}H_{24}$	Undecane	0.5	0.2	0.3	≥ 0.0	0.1	0.1	≥0.0
170	$C_{12}H_{26}$	Dodecane	6.8	13.7	5.5	9.6	4.7	3.9	9.1
212	$C_{15}H_{32}$	Pentadecane	16.1	4.2	17.4	20.8	18.4	14.0	20.3
254	$C_{18}H_{38}$	Octadecane	29.8	30.7	37.2	40.8	38.3	29.5	39.8
296	$C_{21}H_{44}$	Heneicosane	16.0		24.9	20.6	17.5	19.5	17.9
338	$C_{24}H_{50}$	Tetracosane	1.3		3.5		3.8	6.3	2.0
380	$C_{27}H_{56}$	Heptacosane	17.6		5.4		2.9	1.5	3.4
Total percentage of hydrocarbons in the sample headspace			92.2	53.8	95.7	94.3	88.1	75.4	95.0
98	$C_6H_{10}O$	3-Pentene-2-one,4-methyl		0.1					
Total percentage of ketones in the sample headspace				0.1					
212	$C_{14}H_{28}O$	Tetradecanal	0.2					0.4	0.6
226	$C_{15}H_{30}O$	Pentadecanal						0.4	
240	$C_{16}H_{32}O$	Hexadecanal					2.6	13.3	
256	$C_{17}H_{34}O$	Heptadecanal					0.4	0.6	
270	$C_{18}H_{36}O$	Octadecanal					1.6	1.4	
Total percentage of aldehydes in the sample headspace			0.16				4.6	16.1	0.6
92	C_7H_8	Toluene		1.6	0.1	0.1			0.3
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol	1.6						
208	$C_{12}H_{16}O_3$	2-Allyl-5-ethoxy-4-methoxyphenol					4.0	6.0	
220	$C_{15}H_{24}O_2$	2,6-Di-tert-butyl, 4-methylphenol	0.45						
Total percentage of additive-based fragments			2.4		0.2	0.6	4.1	6.0	0.6

Although considered a relatively low temperature to induce significant emission patterns, 90°C was high enough to discern the formulation E (SN1680 + GA-80 + DSTDP) and F (SN1680 + SN1010 + SN4120) from the rest (Table: 6.1-6.6). The two formulations exhibited significantly higher aldehyde emissions comparison with the rest of the group members. Although, apparently the two formulations did not show much variation in their composition from the formulation D (SN1680 + SN1010 + DSTDP) and G (SN1680 + GA-80 + SN4120), only a simple switching of the thioesters across the two pair led to activation of a mechanistic route promoting formation of aldehydes in the former i.e. the formulation E and F. The observation was also in agreement with the CL emissions for the samples (Figure: 5.2 and 5.5). The OIT of the sample E and F (Figure: 5.2 and Table: 5.1), for example, were significantly shorter than that of the sample D and G. The spectra of the former pair also had more heterogeneous emissions and contained wavelengths corresponding to longer chain carbonyls (Table: 5.2., Figure: 5.9-5.12). One can infer that the commonly known synergism between hindered phenols and thioesters is rather an oversimplification of the interactions between the two groups of antioxidants. This interaction between the thioester and hindered phenols is affected by the nature of the individual thioesters and the hindered phenols; SN1010, for example, generated much better stabilisation when used with DSTDP as compared to SN4120, while the opposite was true for GA-80.

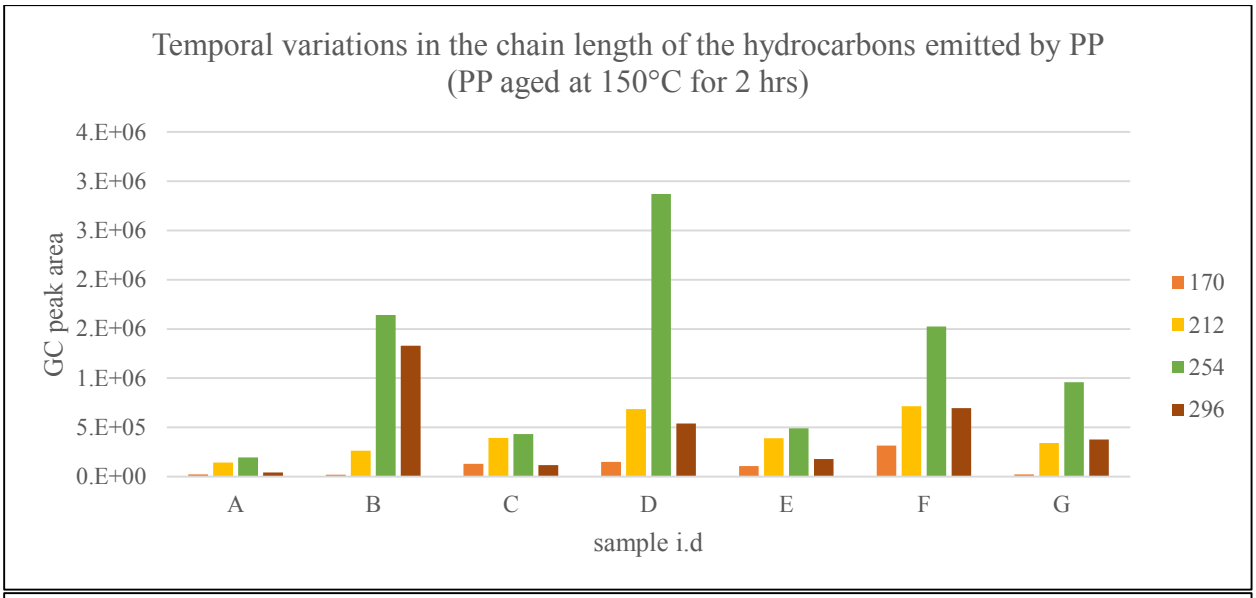
Further, a comparison of the sample B (SN1680 + SN1010) and C (SN1680 + GA-80) with the pair D (SN1680 +SN1010 + DSTDP) and G (SN1680 + GA-80 + SN4120) showed that the addition of thioester does not necessarily make a significant effect on the emission/degradation of the polymer at 90°C (Table: 6.1-6.3). It was also observed that GA-80 provided twice as better stabilisation as SN1010. Again, the better control of GA-80 over the PP emissions was also strengthened by the CL data for the corresponding formulations. The OIT for the formulation stabilised with GA-80, for example, was been observed to be twice as long as that of the one stabilised with SN1010 (Figure: 5.2).

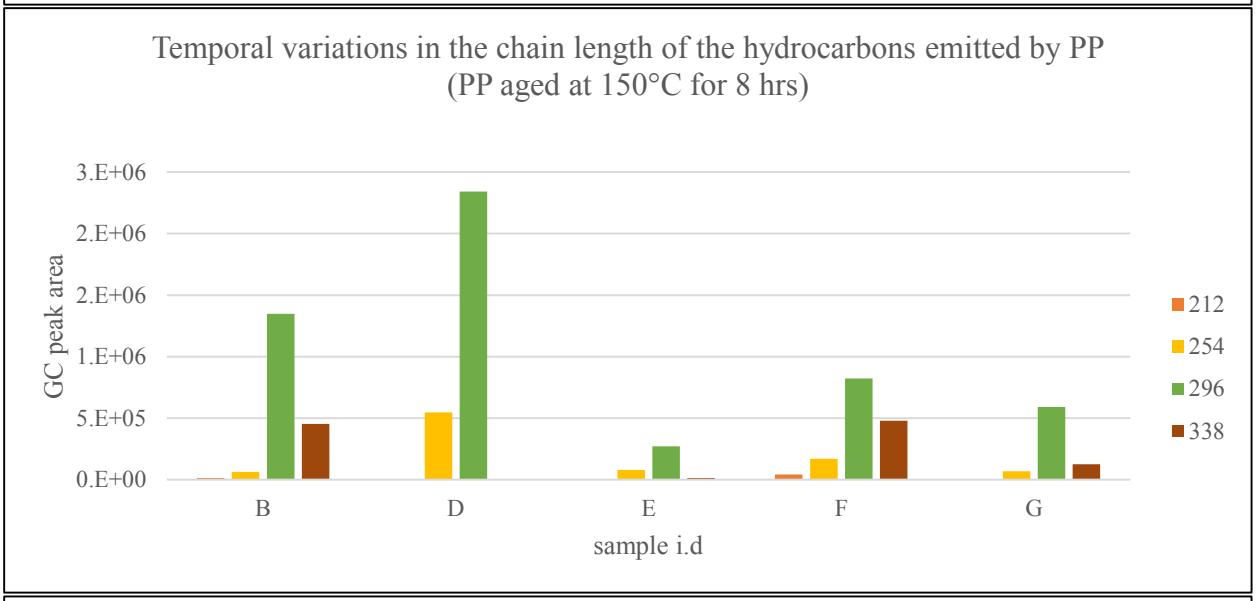
Relatively low stabilisation capacity of SN1010, as far as the results of the current study are concerned, can be attributed to the physical properties of the antioxidant. The antioxidant is, for example, a thermally labile compound with a bulky physical structure (Figure: 2.1). Thermal degradability can cause fast concentration depletion through evaporation of low molecular weight degradation products generated by the antioxidant. The bulky and branched structure,

similarly, can limit mobility and hence diffusion of the antioxidant across a polymeric matrix. At 90°C, benzene, xylene, toluene and 2, 6-bis(1, 1-dimethylethyl) phenol were the main aromatic degradation products in the Group: 1 formulations. The potential sources of these compounds include SN1680 and SN1010, as both contain alkyl substituted aromatic components in their structures. Since all samples, except the sample A, in the Group:1 contained SN1680 and SN1010 in them, the accurate source assignment was more than simple at this stage (Figure: 7.1-7.2), but not impossible. In any further works, especially targeted on the antioxidant degradation in PP, this aspect is worth investigation. To sum it up, the emissions at 90°C for the Group:1, were relatively low but had well defined the patterns that were also observed at higher ageing temperatures as well and were confirmed by the CL analysis of the molten state of the samples in general (Chapter: 5).

For the Group: 1 formulations, increase in the ageing temperature of PP to 120°C, led to an increase in the emissions of the hydrocarbon, and antioxidant degradation products i.e. aromatics. The emissions of ketones at this temperature remained relatively stable with acetone and 3-pentene-2-one, 4-methyl, again the only ketones detected among the emissions (Table: 6.4-6.6). Aldehydes emissions from the formulation E and F were present as predominant carbonyl emissions, but in more diverse molecular range i.e. longer chain aldehydes were detected than at 90°C, while their relative proportion decreased slightly. As far as degradation of the antioxidants is concerned, 4-methyl-2, 6-di-tertbutylphenol and 2-Allyl-5-ethoxy-4-methoxyphenol, were detected in the formulation D and A, in addition to the usual benzene, toluene, xylene and 2, 6-bis (1, 1dimethylethyl) phenols. Overtime, the number and relative concentration of the antioxidant degradation products also increased significantly.

Variation among the formulations was also evident at 120°C. The high aldehyde based emissions was observed again mainly for the formulation E and F during the first 2 hrs, and by all six formulations by the end of the 20 hrs of ageing, while the ketonic emissions were still relatively small across the group. There was an increase in the antioxidant fragment overtime. The antioxidant fragmentation were again low for the formulations containing GA-80. The formulation C (SN1680 + GA-80) and G (SN1680 + GA-80 + SN4120), for example, showed the least antioxidant-based emissions. Like the emissions at 90°C, no alcohols, esters and acids were detected at any stage by any of the formulations at 120°C.





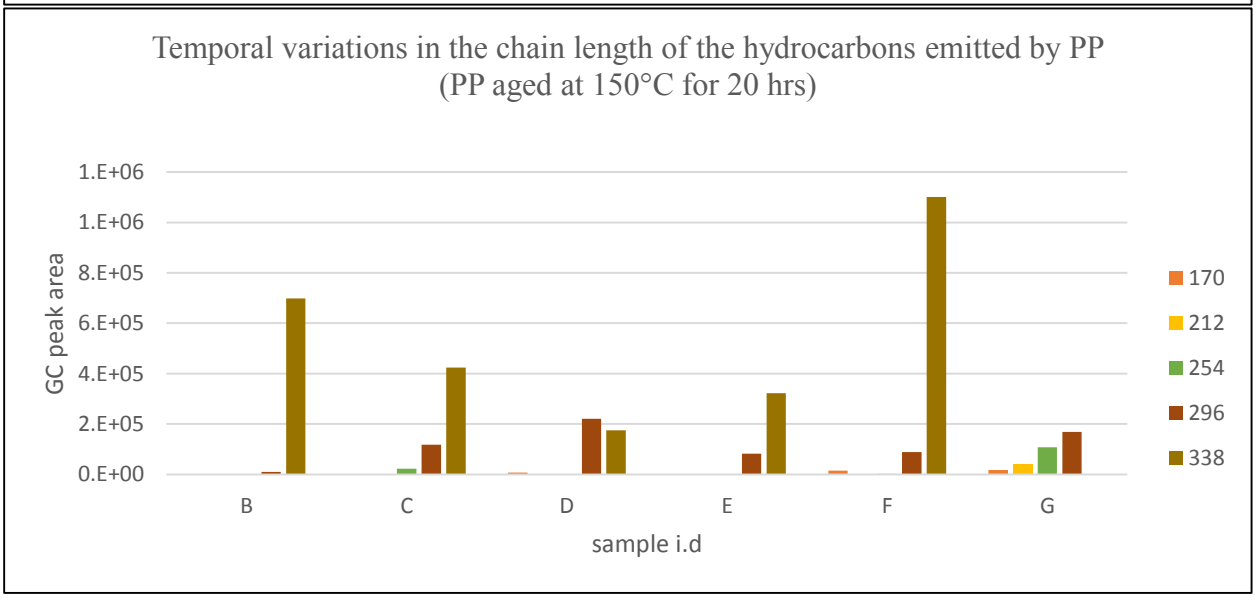


Figure: 6.4. Thermal and temporal variations in hydrocarbon emissions in the formulations A-G.

(170 (dodecane), 212 (pentadecane), 254 (octadecane), 296 (heneicosane), and 338 (tricosane)).

Table: 6.4. Emissions from the formulations A-G after ageing at 120°C for 2 hrs.

Analytical technique			**SSPME-GC-MS**						
Ageing temperature (°C)			**120**						
Ageing time (hrs)			**2**						
Sample i.ds			**A**	**B**	**C**	**D**	**E**	**F**	**G**
m/z	**Formula**	**Names of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS traces**						
44	CO_2	Carbon dioxide	1.51	1.6	2.58	1.55	2.44	2.81	6.93
56	C_4H_8	Isobutylene	0.1	0.09	0.15	0.05	0.15	0.22	0.38
72	C_5H_{12}	Pentane	0.09	0.03	0.05	0.02	0.05	0.08	0.2
86	C_6H_{14}	Hexane and isomers	0.92	1.68	2.11	1.04	2.26	2.31	2.31
100	C_7H_{16}	Heptane	0.03	0.1		0.04			
114	C_8H_{18}	Octane	1.03	0.25	0.16	0.18	0.27	0.14	
128	C_9H_{20}	Nonane	5.7	6.52	3.32	4.12	4.38	3.95	0.38
142	$C_{10}H_{22}$	Decane	0.3	0.56		0.45			
156	$C_{11}H_{24}$	Undecane	2.19	0.26	0.41	0.14	0.52		
170	$C_{12}H_{26}$	Dodecane	24.51	30.22	16.42	24.05	20.66	18.5	0.66
212	$C_{15}H_{32}$	Pentadecane	45.13	48.44	47.04	45.4	47.2	41.08	7.3
254	$C_{18}H_{38}$	Octadecane	11.06	3.92	23.77	18.17	9.17	10.72	13.86
296	$C_{21}H_{44}$	Heneicosane					3.07	2.63	26.2
338	$C_{24}H_{50}$	Tetracosane					1.36	4.47	22.48
380	$C_{27}H_{56}$	Heptacosane							19.24
Total percentage of hydrocarbons in the polymer headspace			91.51	93.34	93.82	94.47	89.56	84.51	93
94	?	?	0.05	0.06	0.06	0.09	0.05	0.16	0.52
92	C_7H_8	Toluene	6.88	4.55	2.01	2.55	2.97	0.5	
106	C_8H_{10}	Xylene			1.52		0.19		
Total percentage of aromatics in the polymer headspace			6.88	4.55	3.53	2.55	3.16	0.5	
58	C_3H_6O	Acetone							1.14
98	$C_6H_{10}O$	3-Pentene-2-one,4-methyl		0.16		0.03			
Total percentage of ketones in the polymer headspace				0.16		0.03			1.14
72	C_4H_8O	Tetrahydro, furan		0.02		0.03		0.09	
240	$C_{16}H_{32}O$	Hexadecanal					0.47	0.59	
256	$C_{17}H_{34}O$	Heptadecanal						1.3	
270	$C_{18}H_{36}O$	Octadecanal					1.52		
284	$C_{19}H_{38}O$	Nonadecanal						5.74	
298	$C_{20}H_{40}O$	Dodecanal						0.34	
312	$C_{21}H_{42}O$	Tridecanal						2.18	
Total percentage of aldehydes in the polymer headspace							1.98	10.15	
220	$C_{15}H_{24}O_2$	4-Methyl-2,6-di-tert-butylphenol				0.13			
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol		0.15		1.07	0.39		
?	?	?					2.41		
?	?	?						0.35	
?	?	?						1.4	
Total percentage of additive fragments in the polymer headspace			0.11	0.21	0.06	1.36	2.85	1.91	

Table: 6.5. Emissions from the formulations A-G after ageing at 120°C for 8 hrs.

Analytical technique			**SPME-GC-MS**					
Ageing temperature (°C)			**120**					
Ageing time (hrs.)			**8**					
Sample i.d			**A**	**B**	**C**	**D**	**E**	**F**
m/z	**Formula**	**Names of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS**					
44	CO_2	Carbon dioxide	1.2	1.3	2.6	2.1	1.6	1.3
56	C_4H_8	Isobutylene			0.2		0.2	0.1
72	C_5H_{12}	Pentane			0.1		0.1	≥0.0
86	C_6H_{14}	Hexane and isomers			0.1		≥0.0	0.1
114	C_8H_{18}	Octane		0.1		0.1		0.1
128	C_9H_{20}	Nonane	0.9		1.5	0.7	0.2	0.4
112	C_8H_{16}	Octene	0.1	0.3	0.1	0.3	0.1	0.3
156	$C_{11}H_{24}$	Undecane	0.4		0.3		0.1	
170	$C_{12}H_{26}$	Dodecane	6.4	6.3	4.3	4.4	1.9	5.2
212	$C_{15}H_{32}$	Pentadecane	20.0	21.4	18.5	15.4	12.1	19.5
254	$C_{18}H_{38}$	Octadecane	61.9	63.2	64.0	59.5	58.2	65.1
296	$C_{21}H_{44}$	Heneicosane	5.0	3.4	3.4	8.6	5.2	1.9
338	$C_{24}H_{50}$	Tetracosane	2.3	1.4	4.9	7.1	5.5	5.3
Total percentage of hydrocarbons in the polymer headspace			96.8	96.1	97.3	96.0	83.6	98
Total percentage of unidentified contents in the polymer headspace			1.6	0.5		0.1		
94		?					0.1	0.1
114	C_4H_8O	Tetrahydro, furan	0.1	0.5		≥0.0	≥0.0	
226	$C_{15}H_{30}O$	Pentadecanal					0.5	0.5
240	$C_{16}H_{32}O$	Hexadecanal					0.7	
254	$C_{17}H_{34}O$	Heptadecanal					1.6	
268	$C_{18}H_{36}O$	Octadecanal	0.2				6.6	
282	$C_{19}H_{38}O$	Nonadecanal					0.5	
296	$C_{20}H_{40}O$	Dodecanal					2.7	
Total percentage of aldehydes in the polymer headspace			0.2				12.6	0.5
220	$C_{15}H_{24}O$	2,6-Di-tert-butyl, 4-methylphenol		0.1				
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol		0.2		0.2		
220	$C_{14}H_{20}O_2$	2,6-Di-tert-butyl-1, 4-benzoquinone		1.4		1.5		
Total percentage of additive-based fragments in the polymer headspace			67	1		1.7	2.1	

Table: 6.6. Emissions from the formulations A-G after ageing at 120°C for 20 hrs

Analytical technique			**SPME-GC-MS**						
Ageing temperature (°C)			**120**						
Ageing time (hrs.)			**20**						
Sample i.d			**A**	**B**	**C**	**D**	**E**	**F**	**G**
m/z	**Formula**	**Names of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS**						
44	CO_2	Carbon dioxide	2.0	2.2	2.3	2.5	1.8	1.6	1.5
56	C_4H_8	Isobutylene	0.2	0.1		0.2	0.2	0.1	0.1
72	C_5H_{12}	Pentane	0.1	0.1	0.2	0.1	0.3	0.5	0.1
170	$C_{12}H_{26}$	Dodecane	0.9						1.7
212	$C_{15}H_{32}$	Pentadecane	3.0	2.3	2.6	1.4			2.3
254	$C_{18}H_{38}$	Octadecane	17.1	30.5	15.6	11.2	14.6	9.7	21.9
296	$C_{21}H_{44}$	Heneicosane	67.7	47.5	78.0	70.2	44.5	50.8	58.1
338	$C_{24}H_{50}$	Tetracosane	2.0	7.6		4.0	6.1	9.9	5.7
380	$C_{27}H_{56}$	Heptacosane	2.5	6.1		5.0	5.3	3.3	4.8
Total percentage of hydrocarbons in the polymer headspace			93.5	94.2	96.4	91.9	71.0	74.3	94.7
94	?	?	0.1	0.1		0.2	0.2		
58	C_3H_6O	Acetone							0.8
226	$C_{15}H_{30}O$	Pentadecanal						1.1	
240	$C_{16}H_{32}O$	Hexadecanal							0.2
254	$C_{17}H_{34}O$	Heptadecanal					0.3	0.8	
268	$C_{18}H_{36}O$	Octadecanal	0.7		0.5	0.2	9.0		
282	$C_{19}H_{38}O$	Nonadecanal	0.3			0.2	1.4	12.7	
296	$C_{20}H_{40}O$	Dodecanal	0.83	0.86		1.36	5.82	5.0	0.6
Total percentage of aldehydes in the polymer headspace			1.8	0.9	0.5	1.8	16.6	19.4	0.9
138	$C_8H_{10}O$	1,2-Dimethoxy benzene							≥0.0
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol		0.4		0.4			0.1
220	$C_{15}H_{24}O$	4-Methyl-2,6-di-tert-butylphenol		1.9					
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol				0.5			0.97
208	$C_{12}H_{16}O_3$	2-Allyl-5-ethoxy-4-methoxyphenol	1.8		0.8	1.7	5.6	0.8	0.7
220	$C_{14}H_{20}O_2$	2,6-Di-tert-butyl-1, 4-benzoquinone		0.2					
220	$C_{15}H_{24}O$	4-Methyl-2,6-di-tert-butylphenol					4.2	3.9	0.3
Total percentage of additive-based fragments in the polymer headspace			1.9	2.7	0.8	2.8	10.5	4.7	2.1

The third series of emission experiments for the Group: 1 formulations, conducted after ageing the samples at 150°C, generated the most important data set representing thermo-oxidative degradation of the polymer in a more pronounced way (Table: 6.7-6.9). Although still in their solid-state, ageing the polymeric formulations at 150°C generated a wide range of ketones, aldehydes, acids, alcohols, esters, and furans. The concentration and range of the antioxidants based degradation products also increased many folds. The most obvious of the changes observed at 150°C was the complete degradation of the formulation A, which occurred within 8 hrs of ageing; the formulation physically turned into a yellow brittle mass and emitted very profusely. SN1680 commonly used as a processing stabiliser, demonstrated poor resistance against thermo-oxidative degradation of PP at 150°C. The emissions from the sample A complex in its nature (Figure: 6.5). A major portion of the chromatogram for the emission from the sample i.e. 51.21% of the total emissions, could not be identified at this stage, however, the unidentified peaks were mainly the oxidation products, e.g. esters, acids and ketones etc. The peaks that could be assigned for the chromatogram of the formation A were mainly carbonyl and a relatively very small proportion i.e. 17%, of the total emissions consisted of hydrocarbons. Hence, 150°C proved to be a threshold beyond which the polymer started to degrade more intensively. Although proven to be a good processing stabiliser for polyolefin, SN1680, like many other member of phosphite based antioxidants is unable to stay inside the polymeric matrix, and is lost at early stage during extrusion. The retention of SN1680 has been reported to increase significantly in presence of hindered phenols [27].

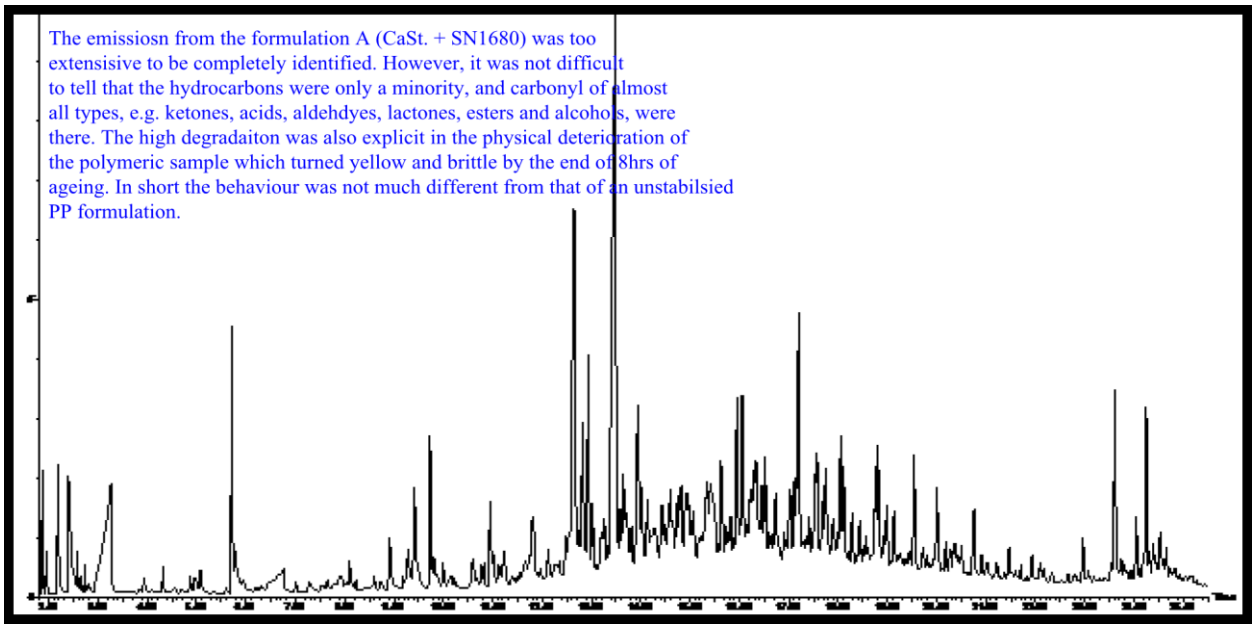


Figure: 6.5. Degradation of PP stabilised with phosphite-based antioxidant only (SN1680).

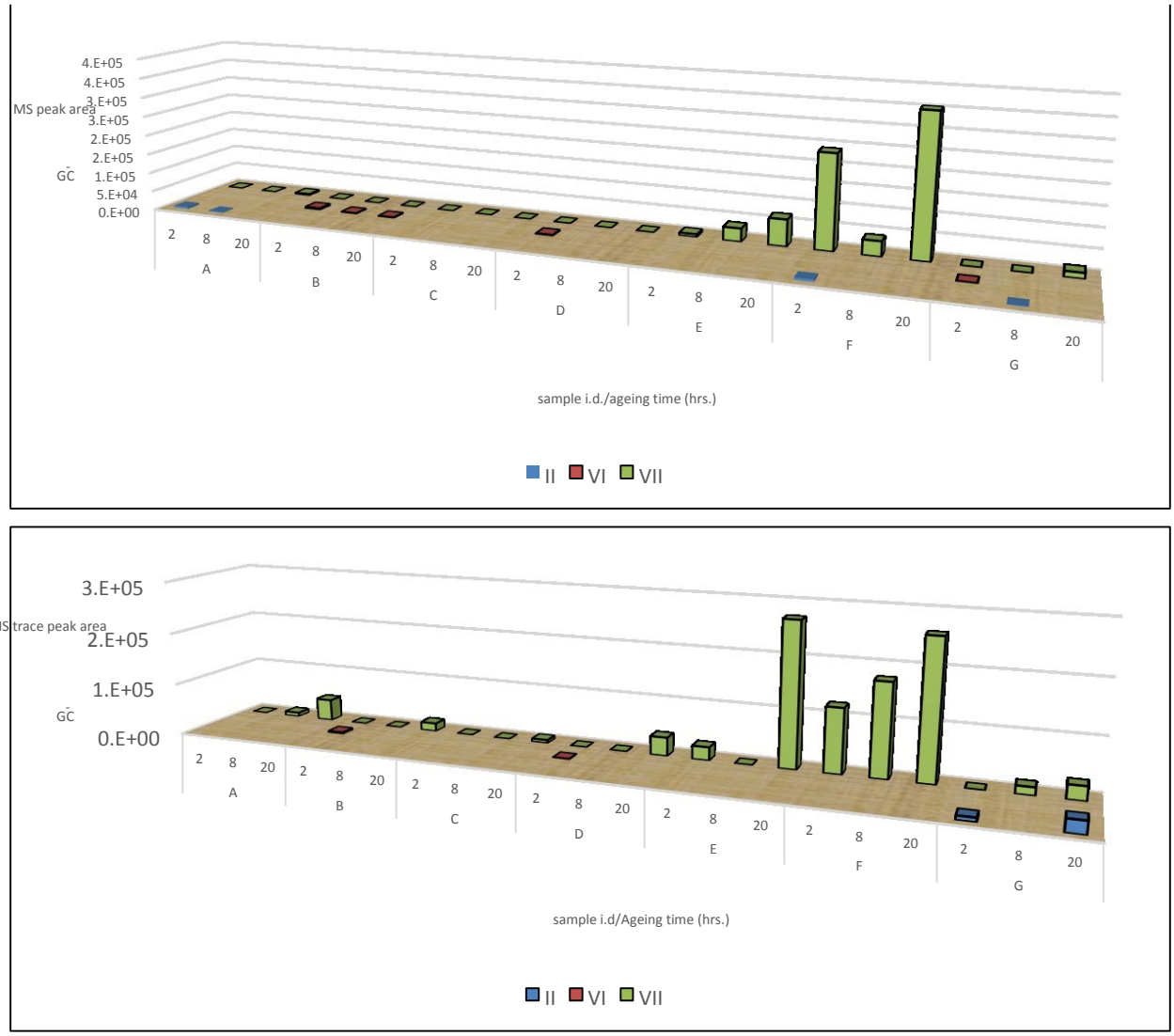


Figure: 6.6. The key carbonyls emitted by the formulation A-G. *(II: formic acid, VI: 3-pentene2-one, 4-methyl, and VII: aldehydes).*

In the carbonyl group, other than the simple methyl ketones, several main-chain ketones and diketones were also identified, while the range of the aldehydes increased from C12-C218 for 90°C and 120°C to C12-C22 for 150°C. Further, a wide range of different types of antioxidant degradation products were detected in substantial proportion (Table: 6.7-6.9 and 7.2). As has been confirmed from the degradation products of the antioxidant analysed at its own i.e. outside the PP matrix, these degradation products were mainly the fragments of hindered phenols and the phosphite-type antioxidant (SN1680). Hence, it was explicit that at 150°C the loss of stabiliser, in the form of low molecular weight degradation products, increased significantly. One important conclusion that can be drawn at this stage is that temperature affects degradation of PP directly and indirectly: firstly, by facilitating the degradation of the polymer itself, and

secondly, through the loss of stabilisers in form of their degradation products. Under depleted concentration of antioxidants, the polymer loses its resistance to thermo-oxidative degradation. The temporal effect on the emissions was simply an increase in the range and relative proportion of the oxidation products of PP, e.g. ketones, aldehydes, acids, esters.

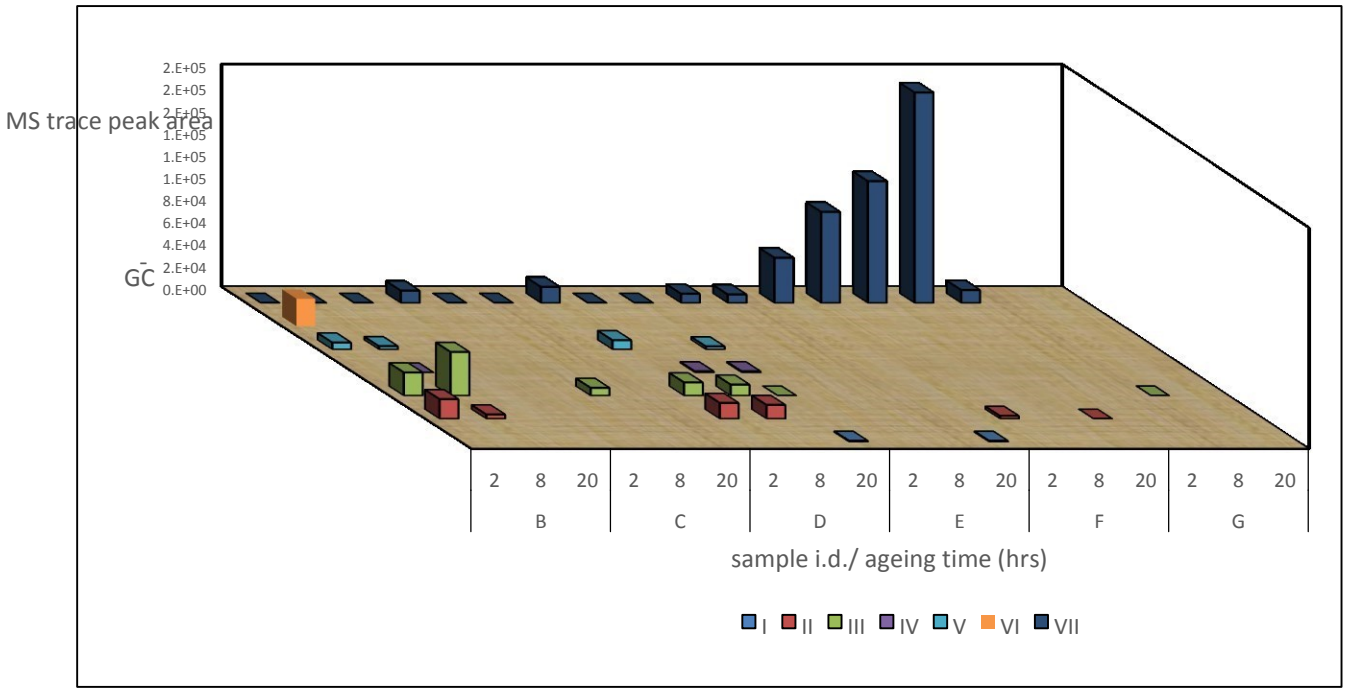


Figure: 6.7. Comparison of the important Key volatile compounds in the formulations B-G aged at 150°C for 20 hrs. (*I: formic acid, II: acetone, III: acetic acid, IV: methyl acrolein, V: 2, 4-pentanedione, VI: 3-pentene-2-one, 4methyl and VII: aldehydes (C4-C12)*).

At 150°C, mutual differences among the emissions from the formations A-G, were also more vivid. While the formulations E and F were still the main source of aldehyde emissions as well as the ketonic emissions right from the first 2 hrs of ageing, almost no carbonyl emissions were detected in the headspace of the formulation C (SN1680 + GA-80) and G (SN1680 + GA-80 + SN4120). The antioxidant-based emission were also negligible (except after 20 hrs when a small amount of emission was detected) for the formulation C and G. It will not be wrong to infer that low loss and greater retention of the additive inside the polymer matrix has played its part in providing high stabilisation against oxidation of the polymer in the formulation C and G. It was also clear that, of the two hindered phenols, GA-80 is much better at stabilisation even at high temperature, e.g. the better stabilisation of the formulation C (SN1680 + GA-80) than SN1010 in the formulation B (SN1680 + SN1010). The formulation B also emitted antioxidant based products in significantly higher proportion. The better stabilisation of GA-80 can be

attributed to its relatively smaller structure, capable of better mobility through the matrix, and high thermal stability i.e. low degradation and hence high retention within the matrix. It is at 150°C that the formulation A started to emit a range of furans in significant proportion i.e. > 2% of the total emissions from the formulation.

Table: 6.7. Emissions from the formulations A-G after ageing at 150°C for 2 hrs.

Analytical techniques			**SPME-GC-MS**						
Ageing temperature (°C)			**150**						
Ageing time (hrs.)			**2**						
Sample i.d			A	B	**C**	**D**	**E**	F	G
m/z	**Formula**	**Names of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS**						
44	CO_2	Carbon dioxide	1	1	5.3	0.5	0.8	1.3	1.1
56	C_4H_8	Isobutylene	0.3	0.2	0.2	0.1		0.0≥	≥0.1
72	C_5H_{12}	Pentane	1.3	0.09					
86	C_6H_{14}	Hexane and isomers	6.3	2.4	2	5.2	0.9	0.5	2.7
100	C_7H_{16}	Heptane	*		0.1				
114	C_8H_{18}	Heptane, 4-methyl	0.2	0.2					
100	C_7H_{16}	Hexane,2-methyl	*			0.3			
114	C_8H_{18}	Octane	*		0.1		0.1	0.1	
128	C_9H_{20}	Nonane	2	0.5	1.9	2.7	0.6	0.4	0.5
112	C_8H_{16}	Octene			0.2		0.1	0.2	
156	$C_{11}H_{24}$	Undecane	0.3	0.2	0.3	0.3	0.3	0.4	
170	$C_{12}H_{26}$	Dodecane	3.9	0.4	10.2	3.1	8.6	9	1.1
212	$C_{15}H_{32}$	Pentadecane	25.1	5.81	30.87	14.33	31.1	20.49	20.7
254	$C_{18}H_{38}$	Octadecane	33.1	33.9	30.5	50.2	29.2	36.8	47.8
Total percentage of hydrocarbons in the polymer headspace			72.5	43.7	76.5	76.1	71	68	73
60	$C_2H_4O_2$	Acetic acid	5.1	0.5		0.25			
58	C_3H_6O	Acetone	2.9	0.4		0.3		0.1	
86	$C_5H_{10}O$	2-Butanone, 3-methyl		0.1					
100	$C_5H_8O_2$	2,4-Pentanedione	1.7	0.1		0.2			
98	$C_6H_{10}O$	3-Pentene-2-one,4-methyl	0.5	≥0.0					
Total percentage of ketones in the polymer headspace			5.1	0.7		0.5		0.1	
96		2,4-Dimethylfurane	0.5	0.3		0.1		≥0.0	
70	C_4H_6O	Methacrolein	1.6						
100	$C_6H_{12}O$	Hexanal						0.1	
128	$C_8H_{16}O$	2-Ethyl, hexanal						0.1	
114	$C_7H_{14}O$	Heptanal						0.2	
128	$C_8H_{16}O$	Octanal				0.3	0.1	0.3	
142	$C_9H_{18}O$	Nonanal			0.9		0.3	0.4	
166	$C_{14}H_{28}O$	Tetradecanal							0.7
170	$C_{10}H_{20}O$	Decanal					0.2	0.4	
226	$C_{11}H_{22}O$	Undecanal						0.2	
240	$C_{12}H_{24}O$	Dodecanal					0.1	0.3	
Total percentage of aldehydes in the polymer headspace			1.1	0.1			0.3	1	0.7
92	C_7H_8	Toluene	7.9	0.1	2.6	0.8	1.9	0.4	0.3
106	C_8H_{10}	Xylene			2.1		0.2		
120	C_9H_{12}	Benzene, propyl		*				*	

138	$C_6H_{10}O_2$	1,2-Dimethoxy benzene		*					
208	$C_{12}H_{16}O_3$	2-Allyl-5-ethoxy-4-methoxyphenol		1.2					
220	$C_{15}H_{24}O$	4-Methyl-2,6-di-tert-butylphenol		0.1					
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol	0.8	0.3		0.2	1		0.5
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol	1						
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol	1.7					0.1	
208	$C_{12}H_{16}O_3$	2-Allyl-5-ethoxy-4-methoxyphenol		2.4					
220	$C_{14}H_{20}O_2$	2,6-Di-tert-butyl-1, 4-benzoquinone		9.4			0.1	0.2	
168	$C_9H_{12}O_3$	1,2,3-Trimethoxybenzene		1.5					
248	$C_{30}H_{46}O_2$	2,6-Di-tert-butyl-4-isopropyl phenol		9.2					
236	$C_{15}H_{24}O_2$	2,6-Di-tert-Butyl-4-Hydroxymethylphenol	0.1		0.2				
Total percentage of additive-based fragments			11.6	24.2	4.9	1.1	2.1	0.7	0.8

Table: 6.8. Emissions from the formulations A-G after ageing at 150°C for 8 hrs.

Analytical technique			**SPME-GC-MS**					
Sample i.d.			**A**	**B**	**D**	**E**	**F**	**G**
Ageing temperature (°C)			**150**					
Ageing time (hrs)			**8**					
m/z	**Formula**	**Name of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS**					
44	CO_2	Carbon dioxide	0.8	0.9	0.3	0.8	2.0	1.7
42	C_3H_6	Propylene	0.5					
56	C_4H_8	Isobutylene	0.2	0.2	0.1			0.2
72	C_5H_{12}	Pentane	≥0.0	≥0.0				0.1
84	C_6H_{12}	1-Pentene, 3-methyl			≥0.0			
86	C_6H_{14}	Hexane			≥0.0	0.1		0.3
84	C_6H_{12}	1-Pentene, 2-methyl	0.1					
100	C_7H_{16}	Heptane	0.1			0.11		
128	C_9H_{20}	Nonane	0.1		0.1			
212	$C_{15}H_{32}$	Pentadecane	4.7	0.5		1.2	2.5	
254	$C_{18}H_{38}$	Octadecane	5.0	2.4	18.1	20.9	10.1	7.5
296	$C_{21}H_{44}$	Heneicosane	7.4	51.8	77.8	70.6	48.8	63.6
338	$C_{24}H_{50}$	Tetracosane		17.4		3.7	28.5	13.5
Total percentage of hydrocarbons in the polymer headspace			19	73	96	97	92	87
		Unidentified	51.2					
46	CH_2O_2	Formic acid	1.8					
60	$C_2H_4O_2$	Acetic acid	4.3	1.5	0.3			
74	$C_3H_6O_2$	Propionic acid	0.1					
86	$C_4H_8O_2$	2-Butenoic acid	1.					
Total percentage of acids in the polymer headspace			7.2	1.5	0.3			
58	C_3H_6O	Acetone	1.0	0.1	0.4			
86	$C_5H_{10}O$	2-Pentanone	0.2					
126	$C_8H_{14}O$	Methyl, heptenone	*					
100	$C_6H_{12}O$	2-Pentanone, 4-methyl	0.1					
84	C_5H_8O	Methyl propenyl ketone	0.2					
98	$C_6H_{10}O$	3-Hexene-2-one	0.2					
100	?	2,4-Pentanedione	1.7	0.1				
101	?	Ketone	0.7					
102	?	Ketone	0.2					

98	$C_6H_{10}O$	3-Pentene-2-one, 4-methyl	≥0.0						
112	$C_7H_{12}O$	3-Hexene-2-one, 3-methyl	1						
142	$C_8H_{14}O_2$	2,4-Heptanedione, 6-methyl	5.9						
116	$C_6H_{12}O_2$	2-Pentanone, 4-hydroxy-4-methyl	0.5						
114	$C_6H_{10}O_2$	4-Methyl-3,4-epoxy-2-pentanone	2.0						
160	$C_{11}H_{12}O$	3-Methyl-4-phenyl-3-buten-2-one	0.4						
Total percentage of ketones in the polymer headspace			14.0	0.3	0.4				
86		2,5-Dimethyl-3,4-hexanediol	0.1						
		Propanoic acid, 2-cyclopropylidene-, ethyl ester	1.3						
72	C_4H_8O	Tetrahydro, furan	≥0.0						
96	C_6H_8O	2,4-Dimethylfurane	0.2	0.2	≥0.0				
110	$C_6H_6O_2$	3-Methyl-5-methyliden-2(5H)-furanone	0.2						
126	$C_7H_{10}O_2$	2(5H)-Furanone,3,5,5-trimethyl	0.2						
138	$C_8H_{10}O_2$	2,5-Dimethyl-3-acetylfuran	1.6						
84	$C_5H_8O_2$	4, 5-dihydro-2-methylfuran	0.5						
Total percentage of esters in the polymer headspace			2.8	0.2	≥0.0				
70	C_3H_4O	Methacrolein	≥0.3	*	≥0.0				
72	C_4H_8O	Butanal	0.1						
100	$C_6H_{12}O$	Hexanal					0.2		
114	$C_7H_{14}O$	Heptanal					0.6		
128	$C_8H_{16}O$	Octanal					0.7		
142	$C_9H_{18}O$	Nonanal					0.9		
156	$C_{10}H_{20}O$	Decanal				0.4	0.8		
170	$C_{11}H_{22}O$	Undecanal				0.4	0.3		
184	$C_{12}H_{24}O$	Dodecanal				0.1	0.7		
198	$C_{13}H_{26}O$	Tridecanal				0.5	0.8		
212	$C_{14}H_{28}O$	Tetradecanal				0.3	0.4		
226	$C_{15}H_{30}O$	Pentadecanal				0.2	1.0		
Total percentage of aldehydes in the polymer headspace			0.4		≥0.0	2.0	6.5		
92	C_7H_8	Toluene		0.2		0.2		0.4	
248	$C_{14}H_{22}O$	2,6-Di-tert-butyl-4-isopropyl phenol	1.2						
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol	1.9						
208	$C_{12}H_{16}O_3$	2-Allyl-5-ethoxy-4-methoxyphenol		1.0					
220	$C_{15}H_{24}O$	2,6-Di-tert-butyl, 4-methylphenol		6.4					
168	$C_9H_{12}O_3$	1,2,3-Trimethoxybenzene		0.3					
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol		1.2					
220	$C_{14}H_{20}O_2$	2,6-Di-tert-butyl-1, 4-benzoquinone		1.5			0.3		
120	C_8H_8O	Phenyl, methyl ketone	0.2						
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol	0.4						12.5
?	?	Aromatic			1.3		0.7		
236	$C_{15}H_{24}O_2$	2,6-Di-tert-Butyl-4-Hydroxymethylphenol							0.2
232	$C_{17}H_{24}O_3$	7,9-di-tert-butyl-1-oxaspirodeca-6,9-diene-2,8-dione		0.3					
240	?	?		0.2					
248	$C_{17}H_{22}O$	2,6-Di-tert-butyl-4-isopropyl phenol		0.8					
248	$C_{17}H_{22}O$	2,6-Di-tert-butyl-4-isopropyl phenol		2.1					
220	$C_{15}H_{24}O$	Phenol,2,6-bis(1,1-dimethylethyl)-4-methyl		1.3			0.4		
176	?	?		5.5			0.2		
292	$C_{35}H_{22}O_3$	3-(3,5-di-tert-butyl-4-hydroxyphenyl) methylpropanoate		3.2					

220	$C_{15}H_{24}O$	Phenol,2,6-bis(1,1-dimethylethyl)-4-methyl		0.3				
Total percentage of additive-based fragments in the polymer headspace			3.6	24.1	3.6		1.6	12.8

Table: 6.9. Emissions from the formulations A-G after ageing at 150°C for 20 hrs.

Analytical technique			**SPME-GC-MS**					
Ageing temperature (°C)			**150**					
Ageing time (hrs.)			**20**					
m/z	**Formula**	**Names of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS**					
			B	**C**	**D**	**E**	**F**	**G**
44	CO_2	Carbon dioxide	3.7	6.6	2.1	0.7	2.4	3.5
42	C_3H_6	Propylene			0.2	0.2		
56	C_4H_8	Isobutylene	0.3	0.5	0.4			0.4
72	C_5H_{12}	Pentane	0.2	0.6	0.1			0.7
86	C_6H_{14}	Hexane and isomers	0.8		0.2			4.8
100	C_7H_{16}	Heptane					0.21	
112	C_8H_{16}	Octene			0.3		0.7	
156	$C_{11}H_{24}$	Undecane			0.5		0.1	
170	$C_{12}H_{26}$	Dodecane			0.8	0.2	0.7	4.0
212	$C_{15}H_{32}$	Pentadecane						9.1
254	$C_{18}H_{38}$	Octadecane		2.8			0.2	17.2
296	$C_{21}H_{44}$	Heneicosane	0.7	14.6	50.6	17.2	5.8	37.7
338	$C_{24}H_{50}$	Tetracosane	51.4	52.5	36.8	67.8	72.7	17.8
Total percentage of hydrocarbons in the polymer headspace			53.5	71.0	89.9	85.4	80.4	91.7
96	C_6H_8O	2,4-Dimethylfurane			0.2			
60	$C_2H_4O_2$	Acetic acid			1.6			
58	C_3H_6O	Acetone					*	
100	$C_6H_{12}O$	Hexanone				*	*	
114	$C_7H_{14}O$	Heptanone					*	
128	$C_8H_{16}O$	Octanone				*	*	
100	$C_5H_8O_2$	2,4-Pentanedione			0.6			
142	$C_9H_{18}O$	Nonanone				*	*	
156	$C_{10}H_{20}O$	Decanone			1.8			
170	$C_{11}H_{22}O$	Undecanone				*	0.1	
184	$C_{12}H_{24}O$	Dodecanone				*		
198	$C_{13}H_{26}O$	Tridecanone				*	0.1	
212	$C_{14}H_{28}O$	Tetradecanone					0.2	
226	$C_{15}H_{30}O$	Pentadecanone					*	
Total percentage of ketones in the polymer headspace					*	*	0.40	
70	C_3H_4O	Methacrolein			0.2			
Total percentage of aldehydes in the polymer headspace						8.5	12.5	
78	C_6H_6	Benzene						0.2
92	C_7H_8	Toluene	0.7	0.4	1.8			2.5
?	?	Aromatic				0.2	0.4	
204	?	?		0.3				
178	?	?		0.6				
140	?	?		0.6				
180	$C_{11}H_{16}O_2$	2-tert-butyl-4-methoxyphenol		0.3				
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl) phenol		0.2	3.1	5.4		0.6

180	$C_{11}H_{16}O_2$	2-tert-butyl-4-methoxyphenol	0.4	1.9				0.2
220	$C_{15}H_{24}O$	2,6-di-tert-butyl-4-methylphenol	1.3				0.5	
248	$C_{30}H_{46}O_2$	2,6-Di-tert-butyl-4-isopropyl phenol	0.3					
232	$C_{17}H_{24}O_3$	7,9-di-tert-butyl-1-oxaspirodeca-6,9-diene-2,8-dione	0.5					
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol		16.7			1.0	
208	$C_{12}H_{16}O_3$	2-Allyl-5-ethoxy-4-methoxyphenol		1.4				
236	$C_{15}H_{24}O_2$	2,6-Di-tert-Butyl-4-Hydroxymethylphenol	0.2					
206	$C_{14}H_{22}O$	2,6-Bis(1,1-dimethylethyl)phenol	0.3					
234	$C_{15}H_{22}O_2$	3,5-Di(t-butyl)-4-hydroxybenzaldehyde	1.6		3.5		1.1	
248	$C_{30}H_{46}O_2$	2,6-Di-tert-butyl-4-isopropyl phenol	2.2					
220	$C_{15}H_{24}O$	4-Methyl-2,6-di-tert-butylphenol	0.9					
276	$C_{17}H_{26}O_3$	3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid	26.3					
248	$C_{30}H_{46}O_2$	2,6-Di-tert-butyl-4-isopropyl phenol			0.8			
292	$C_{35}H_{22}O_3$	3-(3,5-di-tert-butyl-4-hydroxyphenyl)	5.4				1.4	
220	$C_{15}H_{24}O$	Phenol,2,6-bis(1,1-dimethylethyl)-4-methyl	2.2					
Total percentage of additive-based fragments in the polymer			41.7	22.0	7.4	5.4	4.0	3.6

6.1.1.2.2. Emissions from PP stabilised with hindered phenols and thioesters in presence of hydroxylamine as the processing stabiliser

The second group formulations that were analysed during the current study were designed by replacing the processing stabiliser SN1680 in the formulations of the Group: 1 (Table: 2.3) with FS042 (Table: 2.4). It was expected that replacing SN1680 with FS042 will allow an analysis of the effects of SN1680 on the stabilisation of the thioesters and hindered phenols, previously investigated in presence of the phosphite. As evident in the Table: 6.10-6.12, among the main changes that were observed as a result of replacing SN1680 by FS042, aldehydes emissions were significant. There was also a decrease in the ketone emissions, at least for the ageing at 90°C and 120°C. A 10-20% decrease in the hydrocarbon emissions relative to the Group: 1 formulations, in general, was observed. Further, a temporal decrease in the hydrocarbon emissions with time, for all Group: 2, samples was evident.

As shown in the Table: 6.12, ageing at 150°C triggered extensive thermo-oxidative degradation leading to emission of acids, esters, alcohols and relatively higher aldehyde and ketones emissions. The formulation K (FS042 + SN1010 + SN4120) and L (FS042 + GA-80 + DSTDP) generated acids as main oxidation product, while alcohols were generated as the main carbonyl by the formulation L. The formulation J (FS042 + SN1010 + DSTDP) demonstrated a better control over ketone emissions and antioxidant-based emissions. Degradation of the hydroxylamine as nitriles of variable molecular weight were also detected in the headspace of the formulations containing FS042. Further, decrease in the nitriles emissions coincided with relatively better control over the carbonyl emissions by the respective formulations in the Group: 2, e.g. the formulation J.

At 90°C the emissions from the Group: 2. formulations mainly consisted of hydrocarbons (Table: 5.10). The carbonyl emissions for the group: 2 formulations at 90°C were, in general, less than the emissions from the corresponding group: 1 samples. Only the formulation L (FS042 + GA-80 + SN4120) emitted some ketones and aldehydes at this stage. The combination of GA-80 and SN4120 demonstrated the best stabilisation among the Group: 1 samples. The combination however, was less strong than the counterpart formulation in the Group:1. The antioxidant-based fragment in the Group:2, contained substantial nitrile based emissions as well as toluene and xylene. In simple, the emissions from the Group: 2 samples contained less

oxidation products than the corresponding Group: 1 formulations. Increase in ageing temperature to 120°C led to higher carbonyl emissions that increased further, overtime (Table: 6.11).

As far as mutual interactions of the hindered phenols and the thioesters are concerned, the same trends were observed in the Group: 2. Among the hindered phenols, SN1010, for example, demonstrated a synergist and antagonistic relation with DSTDP and SN4120, respectively. Previously strong stabilisation demonstrated by GA-80 in the Group:1 samples, grew significantly weaker relative to SN1010 based samples.

Table: 6.10. Emissions from the formulations H-L after ageing at 90°C for 2, 8 and 20 hrs.

Analytical technique		**SPME-GC-MS**													
Sample i.d.		**H**			**I**			**J**			**K**			**L**	
Ageing temperature		**90**			**90**			**90**			**90**			**90**	
Ageing time		**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**
m/z	**Volatile Name**	**% of the total emissions**													
44	Carbon dioxide	8	3.75	3.27		2.88	2.87	6.86	4.58	3.10	5.44	2.82	2.12	4.86	
94	?	0.20	0.17	0.16				0.20		0.19	0.13	0.11	0.07		
56	Isobutylene	0.49	0.17	0.14		0.19	0.15	0.44	0.20	0.15	0.25	0.16	0.11	0.31	
72	Pentane	0.13	0.10	0.13		0.09	0.15	0.11	0.17	0.18	0.16	0.09	0.11	0.13	
86	Hexane	4.8	1.32	0.26	?	0.72	0.26	4.12	0.96	0.25					
100	Heptane	0.09						0.28			0.39				
114	Octane	0.36						0.27			0.40	0.09		0.19	2.00
128	Nonane	6.24	2.20	0.94		1.4	0.58	5.73	1.98	0.76	5.86	2.43	0.65	5.14	1.65
170	Dodecane	26	23	7.48		9.2	5.66	26.72	11.72	6.37	29.22	10.81	5.82	24.25	11.38
212	Pentadecane	44	31	20.31		23	15.46	47.12	30.25	18.35	47.02	0.00	16.95	42.46	27.44
254	Octadecane	3	40	45.72		49	38.88	4.18	47.62	47.20	3.60	30.28	41.40	3.72	36.67
296	Heneicosane			15.4		11	31.20					45.24	15.75	10.72	9.30
338	Tetracosane			5.29		0.17	3.60			14.71		6.34	8.84		
380	Heptadecane									7.34			2.54		
Total hydrocarbons		86	96.8	95.6		95	96	89	93	95	87	95	92	86	88
92	Toluene	4.84	1.15			0.53		3.81	0.80		4.20	0.79		1.82	0.20
106	Xylene	0.38												0.12	0.38
?	?													*	
?	?													*	
Ketones														<0	
Aldehydes (C18-C20)														2.67	

Figure: 6.8. Thermal and temporal variation in the emissions from the formulations H-L.

Table: 6.11. Emissions from the formulations H-L after ageing at 120°C for 2, 8 and 20 hrs.

Analytical technique		**SPME-GC-MS**														
Sample i.d.		**H**			**I**			**J**			**K**			**L**		
Ageing temperature		**120**			**120**			**120**			**120**			**120**		
Ageing time		**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**	**20**
44	Carbon dioxide	2.4	2.3	2.1	2.27	1.62	1.69	2.35	1.92	1.81	1.91	1.66	1.58	2.58	1.72	2.08
56	Isopropylene	*	*	*	0.14	0.09	0.12	0.07	0.09	0.08	0.06	0.09		0.17		
72	Pentane	*	0.1		0.06	0.08	0.11	0.11	0.08	0.11	0.14	0.07	0.11		0.08	0.12
86	Hexane	2.2		0.14	1.98			1.77			0.09			2.36		0.21
100	Heptane	*														
114	Octane	0.1			0.17			0.07			0.27			0.12		
112	Octene	0.1			0.16			0.07			0.27			0.12		
128	Decane	4.3	0.5		3.63	0.18		3.65	0.22		3.78	0.36		4.59		
?	unidentified	22	5.2	2.9	16.9	2.60		17	2.00		17.5	3.05		23	3.23	
212	Dodecane	53.6	20.9	0.5	41.9	14.9		40	15.6	1.76	46.3	15	1.03	53.5	13.7	1.18
254	Tetradecane	10.2	70	81.8	16.9	52.	9	10	57	22	16	53	15	9.05	63	12
296	Heneicosane				3.50	4.76	44	3.75	2.77	62	0.55	7.28	55		2.62	57.5
338	Tetracosane					3.24	5.15	2.64	2.45	8.60	2.69	0.36	0.41			2.53
380	Heptacosane					2.62	3.96	1.20	0.74	3.72	0.69	3.7	3.7			
Total Hydrocarbons		93	97	85	85	79	62	80	81	98	88	82	75	93	83	73.5
92	Toluene	3.30			1.81			2.12			2.17			1.57		
106	Xylene													0.25		
?	?	0.24			0.21	0.08		0.43	0.07		0.26	0.23		0.48		
?	?	0.17			0.13	0.12		0.22	0.14		0.18	0.07		0.30		
?	?	0.09			0.06	0.08		0.15	0.09		0.06	0.13		0.25		
?	?	0.40			0.08			0.06	0.97		0.15			0.08		
?	?	0.13			0.35			0.09	0.31		0.19			0.09		
?	?	0.58			0.12			0.30			0.30			0.41		
?	?				0.49			0.12			0.11			0.16		
?	?							0.50			0.49			0.68		
?	?	1.61			1.45	0.28	0.00	1.87	1.58		1.73	0.43		2.44		
94	?				0.10	0.11	0.16		*	0.16	0.19					
58	Acetone							0.14			1.00					
Aldehydes (C9-C30)			0.48	12.5	6.35	12	26	9.42	13		2.21	12.2	18			20.6
	Octanitril				2.81			0.47					0.47		15	
	Decanitril								0.52							
	Dodecanitril					4.95	7.04	2.86	0.48		1.57	0.20	0.29			3.68
	Tetradecanitril					1.28	2.37		1.20		0.79	3.30	4.20			
Total Nitrils					2.8	6.24	9.4	3.33	2.19		2.36	3.5	5.0	0	15	3.7

Other than the variations in the relative ratio of the oxidation products, a temporal decrease in the hydrocarbon contents was observed as another important feature of the emissions from the Group: 2 formulations. In the formulation L, for example, the initial > 80% hydrocarbons reduced to 23% by the end of 20 hr ageing of the sample at 150°C. The formulation H (FS042),

similar to the formulation A in the Group: 1, degraded extensively generating a chromatogram too complex to be assigned completely.

Table: 6.12. Emissions from the formulations H-L after ageing at 150°C for 2, 8 and 20 hrs.

Analytical technique		**SPME-GC-MS**													
Sample i.d.		**H**		**I**			**J**			**K**			**L**		
Ageing temperature		**150**		**150**			**150**			**150**			**150**		
Ageing time		**2**	**8**	**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**	**20**
44	Carbon dioxide	2.4	0.8	0.8	2.9	1.4	0.8	1.9	2.	0.5	0.2	0.2	1.3	0.8	0.8
56	Isopropylene			*	0.37	*		0.14	0.2						
86	Hexane	1.4	1.4	0.4			0.1	1.6	3.5	0.03		0.3	0.1		0.01
128	Nonane	2.2	3.4	1.0	0.0	0.0	0.5	9.2	15.6	0.3			0.4		
100	Heptane	0.1	0.3	*				0.4	0.4						
114	Octane	0.1	0.4					9.0	0.23						
170	Dodecane	6.1	4.4	7.7	0.7		6.99	35	7.14	4.39	2.65	0.00	4.0	0.00	0.16
212	Pentadecane	30	44	24.	2.35	4.65	21.3			26			37		
254	Octadecane	33	12.9	35	14.0	2.64	29.2			44.1	11.2	1.62	39	2.81	0.27
296	Heneicosane	14	6.7	21	28	4.31	19.3			2.6	43	2.0	2	25	2.4
338	Tetracosane		1.7	0.8	14.0	25.6	3.56			0.5		20.0	0.5	6.7	20.0
Total percentage of hydrocarbons		87	76	91	60	37	80	55.0	26.8	78.0	56.8	24.4	84	34.8	22.9
96	2,4-dimethyfuran		3.41		0.39			0.17	0.23	0.12					
114			0.10	0.06				0.47	5.07						
?	?														
92	Toluene	2.6	0.09	1.24			1.25	0.20	0.55	0.37			0.08		
106	xylene	*						0.31	1.69						
?	?	0.1	0.06	0.09	0.08	23.94	0.09	0.70	0.66	0.16	1.77		0.19	1.15	
?	?	0.1	0.03	0.11	1.12		0.41	0.34	0.52	0.29	0.34		0.20		
?	?	0.5	0.18	0.10			0.04	10.33	0.47	0.15	0.51		0.06		
?	?	2.8	0.05	0.14			0.07	0.34	0.40	0.04	0.42		0.11		
?	?		0.03	0.22			1.18	1.30	0.29	0.51	0.23		0.36		
?	?		0.05					0.46	0.53	0.16	0.17		0.06		
?	?		0.29					0.52	1.54	1.42	0.10		2.30		
?	?		0.59					5.60	1.89	0.10	0.07		0.09		
?	?		0.11					0.75	0.22	0.14	0.16		0.12		
?	?		0.15					2.06	0.27	0.07	0.23		0.85		
?	?		0.11					1.52	28.31	0.07	0.20		0.36		
?	?		0.09					1.18	0.28	0.05			0.69		
?	?		0.75					0.93	0.37	0.24			3.27		
?	?		0.04					0.69	6.07	0.44					
?	?		0.18					1.38	6.37	0.49					
?	?		1.36					0.09	0.18						
?	?		0.41					3.75	0.58						
?	?		0.33					0.93	1.39						
?	?		0.22					0.46	1.18						
?	?		0.04					0.60	0.59						
?	?		0.20												
?	?											*			
?	?												0.17		
104	Phenyl butenoate						0.30								

?	?											0.06			
120	Benzene, propyl							0.07							
138	2,3,3,5-Tetramethyl-1,4-hexadiene								0.14						
220	2,6-di-tert-butyl-4-methylphenol			0.18	1.33	2.05		0.22					0.07	0.04	
206	2,6-Bis(1,1-dimethylethyl)phenol			*	*										
220	2,6-di-tert-butyl-4-methylphenol			0.73				0.41							
?	?				0.22										
248	2,6-Di-tert-butyl-4-isopropyl phenol					0.56									
234	3,5-di-tert-butyl-4-hydroxybenzaldehyde				*	0.83			1.63	0.48				0.16	
Total percentage of aldehydes		0		<0	<0	0.83			1.6	0.5	0			<0.2	
Total percentage of acids in the headspace									1.3	*			<7.9	<1.8	
Total percentage of alcohols													1.05	1.75	
58	Acetone	*	0.08					0.16					*	0.04	
?	?									*					
72	Butanone												*	*	
86	Pentanone												*		
100	Hexanone												*	*	
98	3-Methyl-cyclopentanone		0.04												
98	3-Methyl-cyclopentanone		0.02												
100	2,4-Pentanedione							0.79	0.39						
100	Hexanone isomer												0.19	*	
?	?									*					
?	?							0.18							
?	?							0.09							
142	Heptanone	0.13		0.08			0.09	0.14					0.04	*	
112	1,4-Cyclopentanetrione								0.18						
114	4-Pentanone, 4,6-dimethyl	0.19					0.08		0.08				0.92		
142	2,7-Octanedione							0.33	0.75						
114	2-Heptanone								0.15						
114	3-Pentanone, 2, 4-dimethyl								0.11						
?	?							1.26							
156	Octanone		0.45										*	0.14	
142	Nonanone		0.52				0.11		0.10				*		
172	Decanone					*									
?	?									*					
?	?									*					
?	?												*		
?	?									*					
?	?									0.70					
?	?									0.43					
?	?									*	*				
		<0	<1	0.1		<0	0.3	<2	<1.4	<1	<0		<1	<0.1	
Total percentage of nitriles					6.90	2.34				8.37	0.95		1.53	13.62	
Total percentage of aldehydes		1.2	0.3	4	27	30.5	15	12.6	33.6	65	0.8		51	59	

6.1.1.2.3. PP stabilised with CaSt, vitamin E and SL1190

The Group: 3 (Table: 2.5) formulations, as mentioned earlier, were unique and important as they were specifically targeted on the CaSt (an antacid), SL1190 (a light stabiliser), and vitamin E (a natural antioxidant). The three candidates of PP stabilisation has only rarely been the focus of research on PP emissions.

Calcium stearate is added to PP as an acid neutraliser, and is a common part of stabilisation packages in commercial applications of the polymer. CaSt at its own showed extensive degradation at 150°C. Its degradation products mainly consisted of a range of acids, aldehydes, ketones, esters, and alcohols (Table: 7.1 and Figure: 8.3-8.4). A careful comparison of the degradation of the CaSt degradation products with the emissions from the PP formulations containing the additive in them showed a strong possibility potential contributions by CaSt toward the emissions from the polymeric samples. An attempt to test the assumption was made by replacing CaSt with ZnO in the formulation N. Emissions from the sample N at 90°C and 120°C, like most of the samples in the current study, were mainly hydrocarbon with only a small proportion of aldehydes and stabiliser-based emissions (Table: 6.13 and 6.14). At thermal effect for ageing the sample at 150°C was observed in the form of high aldehyde content (Table: 6.15). The higher carbonyl content in the emissions from the sample N can however, also be due to absence of a hindered phenol or even the phophite. A fair assessment of the role of the emissions from CaSt, indeed requires two identical formulation with CaSt and ZnO as the only distinguishing features.

The role of the UV-light stabiliser, SL1190 (Figure: 2.1 and Table: 2.1), was very interesting throughout the study. The antioxidant demonstrated good control over degradation in the IR analysis, and a peculiar CL emission pattern. In the emissions analysis, it again ranked among the low emitting samples in the series of the formulations investigated in the current study. Last but not least was the Vitamin E. It is a natural antioxidant with a structure similar to hindered phenols. In combination with DSTDP, the antioxidants generated aldehyde and ketones, which increased in proportion overtime. A more comprehensive overview of the stabilisation behaviour of vitamin E required the antioxidant tested in more varied combinations with other antioxidants, e.g. SN1680, FS042 etc. (Table: 7.1).

Table: 6.13. Emissions from the formulations M-O after ageing at 90°C for 2, 8 and 20 hrs.

Analytical Technique		**SPME-GC-MS**								
Ageing temperature (°C)		**90**								
Sample i.d		**M**			**N**			**O**		
Ageing time		**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**	**20**
m/z	**Names of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS traces**								
44	Carbon dioxide	5.7	2.7	2.0	5.6	2.6	2.0	5.7	1.8	4.2
56	Isopropylene	0.3	0.1		0.3	0.2	0.1	0.4	≥0.0	0.2
72	Pentane	0.1	0.1	0.1	0.13	0.14	0.08	0.1	0.1	0.2
86	Hexane and isomers	3.5	0.6	0.1	3.0	0.7	≥0.0	2.0	0.8	0.1
100	Heptane and isomers					0.17				
114	Octane and isomers				0.4	0.1		0.4		
128	Nonane and isomers	4.9	1.4	0.3	6.1	2.1	0.6	7.0	3.4	1.6
170	Dodecane and isomers	24.5	9.2	4.8	25.4	29.9	4.1	28.3	21.0	8.7
212	Pentadecane and isomers	46.8	25.3	15.2	44.6	32.1	11.6	43.4	36.6	18.8
254	Octadecane and isomers	7.2	50.7	34.7	8.0	5.1	28.2	6.1	31.9	34.9
296	Heneicosane and isomers		4.3	25.0		7.7	11.3			23.8
338	Tetracosane	4.1		4.8			8.8			4.2
380	Heptacosane			4.1			8.1			0.1
Total percentage of hydrocarbons in the polymer headspace		95.2	92.6	89.2	91.3	79.0	72.9	90.1	94.7	92.8
58	Acetone							0.5		1.1
Total percentage of aldehydes in the polymer headspace		0.6	2.6	5.1		11.0	14.3			
Total percentage of nitriles		1.3	2.6	5.7	3.6	7.2	11.1			
92	Toluene	0.7	0.2		2.0	0.4		3.7	4.1	
106	Xylene				0.4	0.5		1.92	0.3	0.1
206	2,6-Bis(1,1-dimethylethyl)phenol								*	*
Total percentage of additive-based fragments		0.7	0.2		2.4	0.8		5.7	4.4	2.1

Table: 6.14. Emissions from the formulations M-O after ageing at 120°C for 2, 8 and 20 hrs.

Analytical technique		**SPME-GC-MS**								
Ageing temperature (°C)		**120**								
Ageing time (hrs)		**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**	**20**
Sample i.ds			**M**			**N**			**O**	
m/z	**Names of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS traces**								
44	Carbon dioxide	2.35	2.40	1.70	2.39	0.94	0.99	1.58	1.57	6.44
56	Methyl, propane	0.11	0.17	*				0.07	0.05	0.35
72	Pentane	*	0.09	0.11				0.03	0.04	0.18
86	Pentane, 3-methyl		1.04		0.12		5.78	0.10	0.12	*
86	Pentane, 2-methyl	0.15	0.14		0.15		1.77	0.13		*
84	1-Pentene, 2-methyl	0.25	0.28		0.06			0.04		*
86	Hexane isomers	1.86	2.04	0.00	1.47	0.00	7.55	1.15	0.12	0.00
100	Heptane		0.08					0.02		
112	Octene	0.98	1.14	0.00	0.34	0.00	0.00	0.34	0.00	0.49
128	Nonane	3.60	1.62	0.00	3.83	0.19	0.00	5.53	0.96	0.00
170	Dodecane	21.92	0.00	1.47	21.57	2.43	1.75	27.44	5.55	1.83
212	Pentadecane	49.37	14.77	0.00	47.93	13.64	0.00	47.66	18.57	7.26
254	Octadecane	18.74	59.87	15.09	9.64	60.09	16.93	10.02	63.39	13.63
296	Heneicosane		7.11	57.21	2.59	1.32	35.80	0.00	5.80	21.12
338	Tetracosane	0.00	0.86	9.11	5.78	6.14	10.60	0.00	0.00	44.84
Total percentage of hydrocarbons in the polymer headspace		98.44	89.79	82.99	94.62	83.81	80.18	93.41	94.60	89.70
58	Acetone									1.06
?	ketone	*			0.18			0.12	0.25	
Total percentage of ketones in the polymer headspace		*	0.11	0.00	0.18	0.00	0.00	0.12	0.25	1.06
?	Acid						1.29			
?	Acid		0.12							
?	Acid	0.08						0.95		
?	Acid	0.37						0.36		
?	Acid								1.06	1.19
92	Toluene	0.61	0.34		1.59			2.47		1.11
106	Xylene	0.00	0.00	0.00	0.39	0.00	0.00	2.12	0.05	0.00
136	1,Cyclohexene-1-methanol							0.08	*	
220	2,6-Di-tert-butylquinone		0.64	*					0.23	
206	2,6-Bis(1,1-dimethylethyl)phenol				*			*	1.93	
234	3,5-di-tert-butyl-4-hydroxybenzaldehyde								*	
276	3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid								0.31	
Total percentage of additive-fragments in the polymer headspace		0.61	0.98	0.00	1.98	0.00	0.00	4.67	2.53	1.11
Total percentage of aldehydes in the polymer headspace			6.18	11.10	0.00	1.44	2.29			
Total percentage of nitriles in the polymer headspace			0.58	6.1	2.3	12.8	23.3			

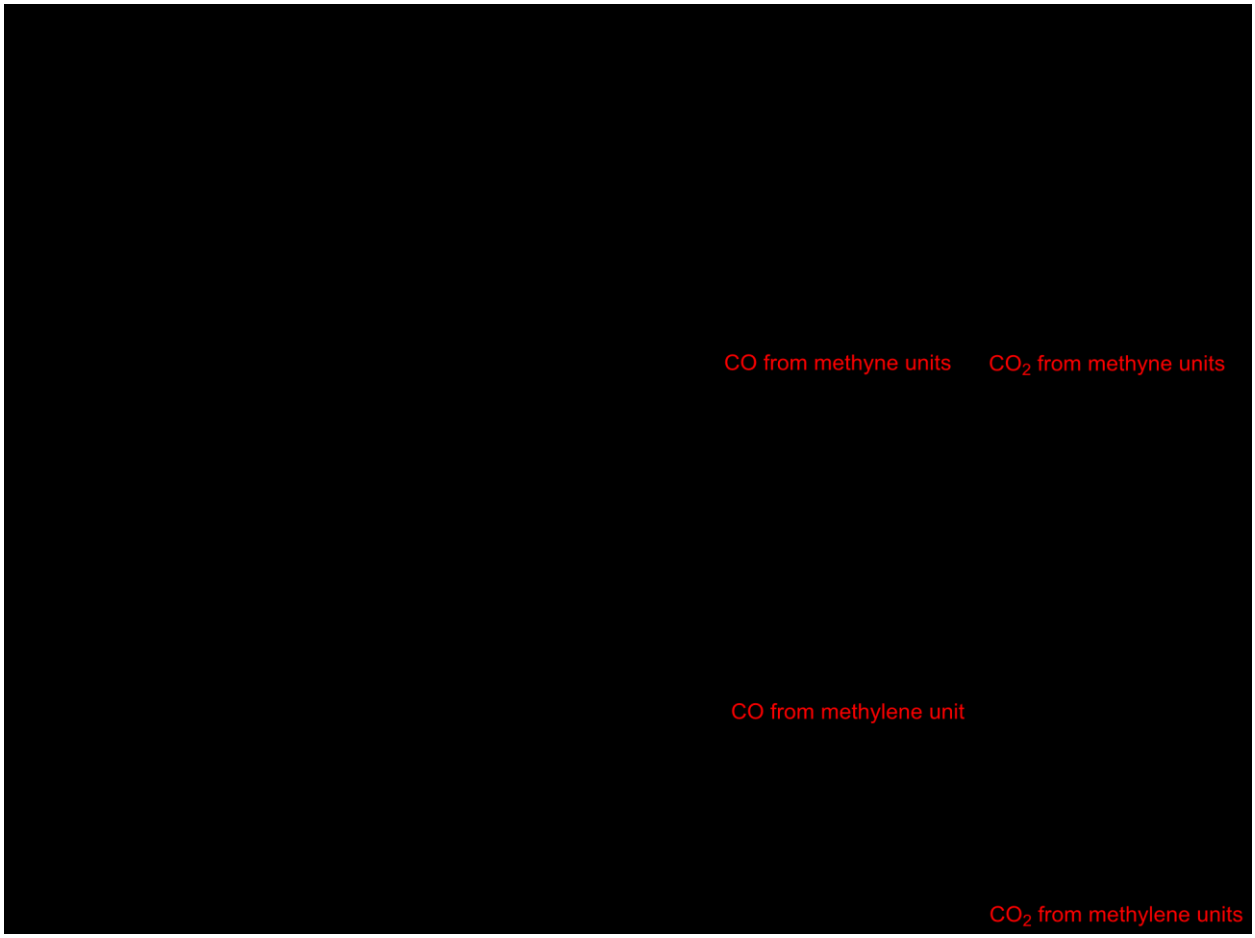
Table: 6.15. Emissions from the formulations M-O after ageing at 150°C for 2, 8 and 20 hrs.

Analytical technique		**SPME-GC-MS**								
Sample i.d.		**M**			**N**			**O**		
Ageing temperature (°C)		**150**			**150**			**150**		
Ageing time (hrs)		**2**	**8**	**20**	**2**	**8**	**20**	**2**	**8**	**20**
m/z	**Name of the volatiles**	**Relative % of the total peak area of the corresponding GC-MS traces**								
44	Carbon dioxide	0.2	0.1	0.3	0.3	2.3	0.1	0.4	1.5	2.7
56	Isopropylene				≥0.0	≥0.0	≥0.0		0.1	0.1
72	Pentane					0.3			≥0.0	0.3
86	Hexane and isomers			0.2		0.5	0.01	<1.59	0.1	1.6
100	Heptane and isomers					0.1				0.2
114	Octane and isomers							*		
128	Nonane and isomers	0.4						1.0		
170	Dodecane and isomers	0.5	0.6		0.5	1.0	0.8	0.5		
212	Pentadecane and isomers	30.1		0.4	12.3	0.3	0.2	12.9		2.2
256	Octadecane and isomers	41.3	15.5	3.1	30.3	2.8	0.4	33.6	28.8	
296	Heneicosane	12.8	76.4	10.0	34.8	32.5	4.1	8.9	62.5	15.9
338	Tetracosane	1.1		48.2	1.3	6.2	16.3	4.3		48.2
Total percentage of hydrocarbons		86.2	92.5	62.0	79.2	43.9	21.9	62.8	91.6	68.5
202								1.6		
70	Butenal								*	0.2
72	Butanal							0.1	0.1	0.5
114	Heptanal			≥0.0	*	0.1	≥0.0			
128	Octanal		0.3	0.2	≥0.0	0.2	0.1			
142	Nonanal	0.3	0.7	0.6	*	0.3	0.2			
156	Decanal		0.5	0.6	0.1	0.3	0.4			
?	?		0.5	0.7	*	0.7	0.7			
184	Dodecanal		0.5	0.6	4.1	14.4	17.7			
?	?		0.6	0.9						
226	Pentadecanal		0.4		2.0	0.8	0.9			
240	Hexadecanal		0.8		3.1	5.6	3.5			
?	?		0.9			0.2	*			
?	?			4.0	1.1	4.8	4.2			
?	?			1.8	2.5	22.4	41.3			
?	?			1.9	0.2	0.7	1.4			
?	?				0.1	0.3	0.6			
Total percentage of aldehydes		0.3	5.3	12.1	13.3	50.9	71.2	0.1	0.1	0.7
60	Acetic acid									0.2
Total percentage of acid (C9-C11)				*						0.2
58	Acetone						*	0.1	0.1	0.5
86	2-Pentanone									0.3
98	4-Hydroxy-4-methylpentanone					0.11				
226	Other ketones			<16.2				14.3		
Total percentage of ketones in the polymer headspace			*	<16.2		0.1	*	<13	0.1	0.8
Total percentage of unidentified content		11.0	0.8	0.9	1.3		1.2	1.2		0.7
Total percentage of nitriles in the polymer headspace				2.0	3.2	2.8	5.6			
78	Benzene									0.2
92	Toluene	0.2			≥0.0			0.5	0.7	2.
106	Xylene							1.1		

220	4-Methyl-2,6-di-tert-butylphenol							0.3
206	2,6-Bis(1,1-dimethylethyl)phenol					4.8	0.7	4.3
192	Neopentyl benzoate					0.1		
172	?					0.3		
220	Phenol,2,6-bis(1,1-dimethylethyl)-4-methyl	0.3	0.8	0.9			0.1	
184	?					2.9	0.5	
204	?					7.4	3.0	1.2
216	?					1.4	1.6	
234	3,5-di-tert-butyl-4-hydroxybenzaldehyde			3.8				
248	2,6-Di-tert-butyl-4-isopropyl phenol			1.6				
Total percentage of additive fragments		0.5	0.8	6.5	0.2	20.3	6.6	8.2

6.1.1.2.4. Carbon dioxide emissions

Carbon dioxide (CO_2) and carbon monoxide (CO) are important products of thermo-oxidative degradation in polyolefin. Previously, CO and CO_2 emissions from PP have been studied through isotopic labelling of the primary (methyl groups), secondary (methylene) and tertiary (methine) carbon sites along the polymeric chain. Various mechanisms were reported for the formation of the two carbon oxides proposing that 2/3 of CO_2 generated by PP at a given point originate from methylene, while only 1/3 from methine carbons of the polymer [123]. In PP, with tertiary carbon chemistry as the major degradation pathways, the higher contribution of the methylene carbon in CO_2 formation require formation of the secondary alkyl radicals through alternative mechanistic routes. The various mechanisms proposed include β-scission of methine and primary alkoxy groups as well as the typical pathways forming the free radical (Scheme: 6.1).



Scheme: 6.1. Formation of CO_2 during degradation of PP [59].

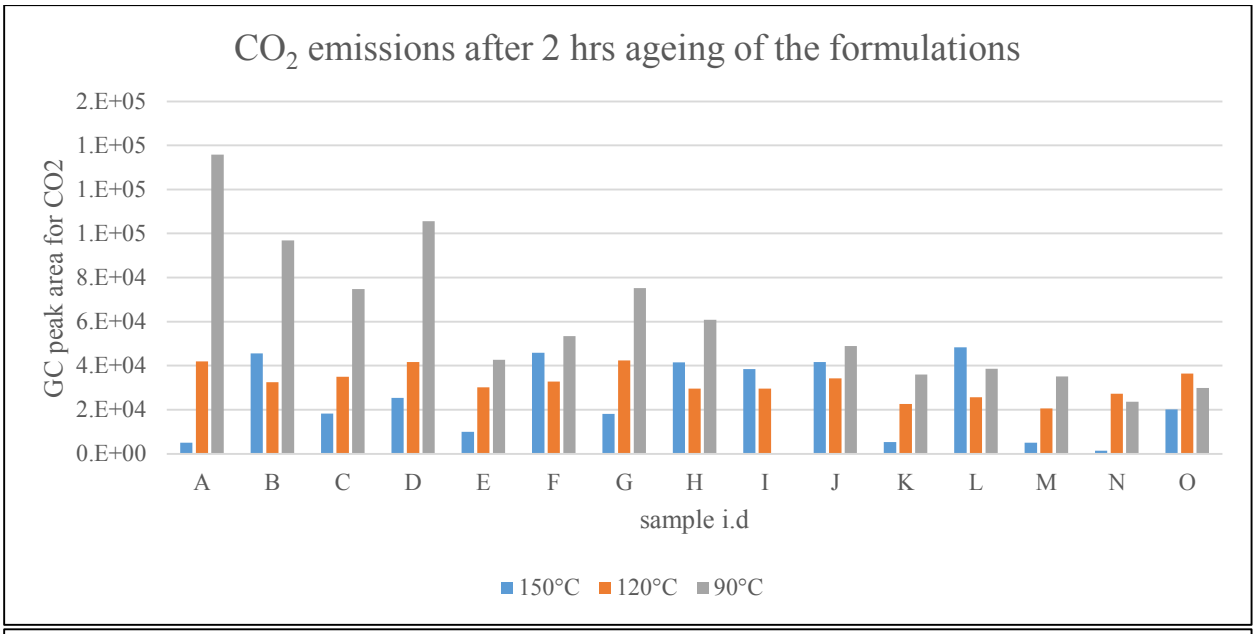
In the context of the above proposed explanation for the formation of CO_2, variations in the relative proportion of the gas emitted by PP formulations can be used to understand the

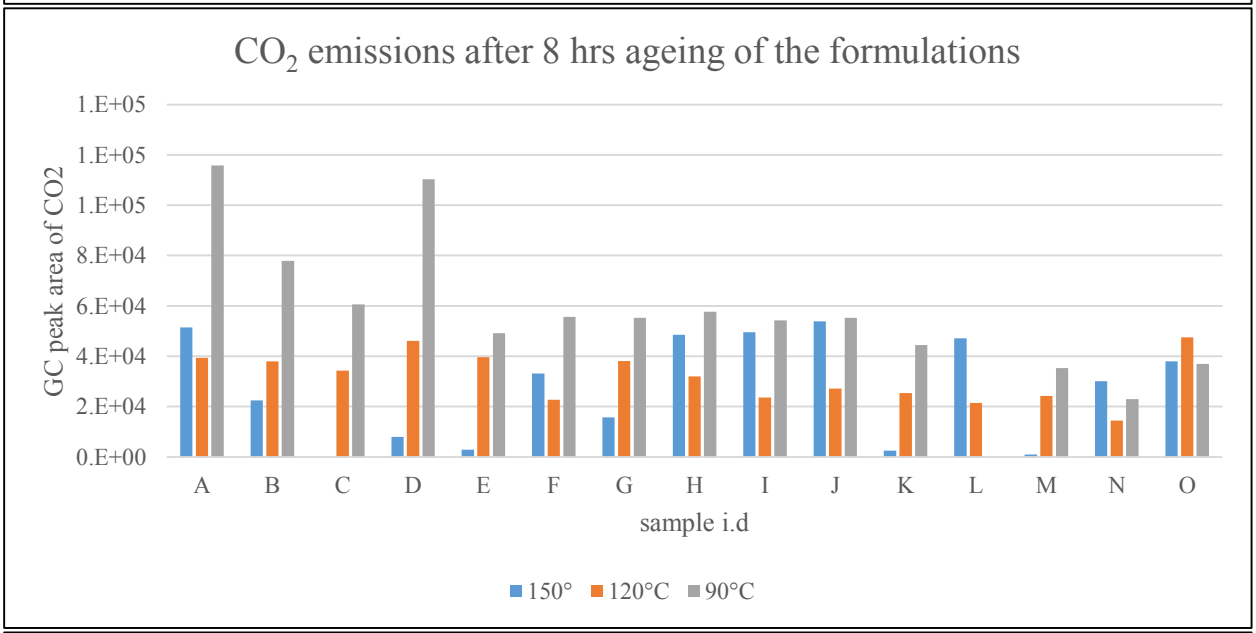
underlying chemistry further. In the current study CO_2 was consistently identified in significant proportion i.e. > 1% of the total emissions at least, amongst the emissions from all formulations. The emissions were consistently observed irrespective the ageing conditions and composition of the stabilisation packages in the formulations. Since the current study was not targeted at CO_2 emission, in particular, the results did suffer from experimental artefacts, and requires to be considered as approximation of the behaviour of the PP formulation.

The CO_2 emissions from the fifteen formulations investigated in the current study, were recorded for 90°C, 120°C and 150°C over a period of 20 hrs. The peak areas of CO2 in the chromatograms are plotted are shown in the Figure: 6.9. It shows that

- CO_2 emission was higher at the lower ageing temperature i.e. 90°C, and decreased as the ageing temperature increased, implying that the methine and methylene radicals are more important at lower ageing temperature.
- There is also variation in the way different stabilisation packages affected the behaviour of the CO_2 emissions by the formulations. The trend of thermal decrease in CO_2 emission was observed in the majority of the formulation, e.g. A, C, D, E, G, K, M, N and O. In the rest, a decrease in the CO_2 emissions as the temperature increased from 90°C to 120°C was followed by an increase as the temperature was further increased to 150°C, e.g. F, H, J and L.

One key issue with the measurement of the CO_2 emissions by the SPME-GC-MS method was that the gas was not only the part of the emissions, it was also introduced into the degradation cell as a part of the air mixture used to age the polymeric samples. The correction for the CO_2 coming from air was done by running an air blank using SPME-GC-MS method under the same experimental conditions as for the samples. The results so far do suggest the CO2 emissions as an important source of data for insight into PP degradation chemistry from a slightly different angle. However, the validity of the current data needs to be ascertained through careful planning of the same experiment, with special reference to the CO_2 measurements during PP degradation.





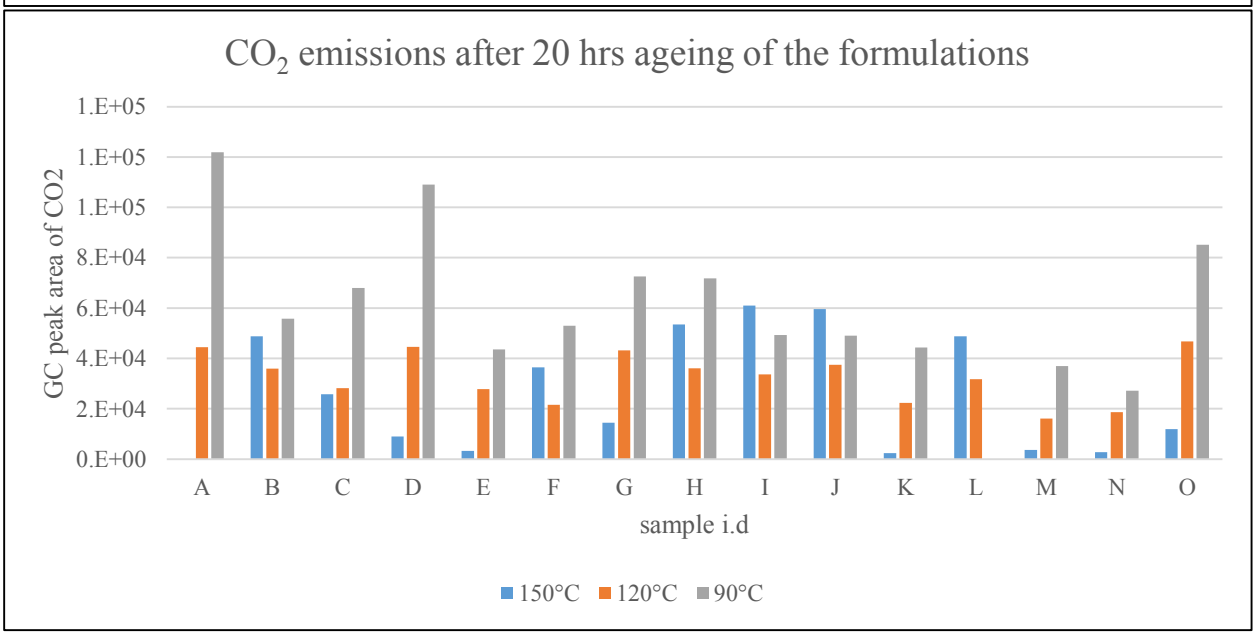


Figure: 6.9. Thermal and temporal variation in CO_2 emissions for the formulations A-O.

6.1.1.3. Chemical mechanisms of PP emissions

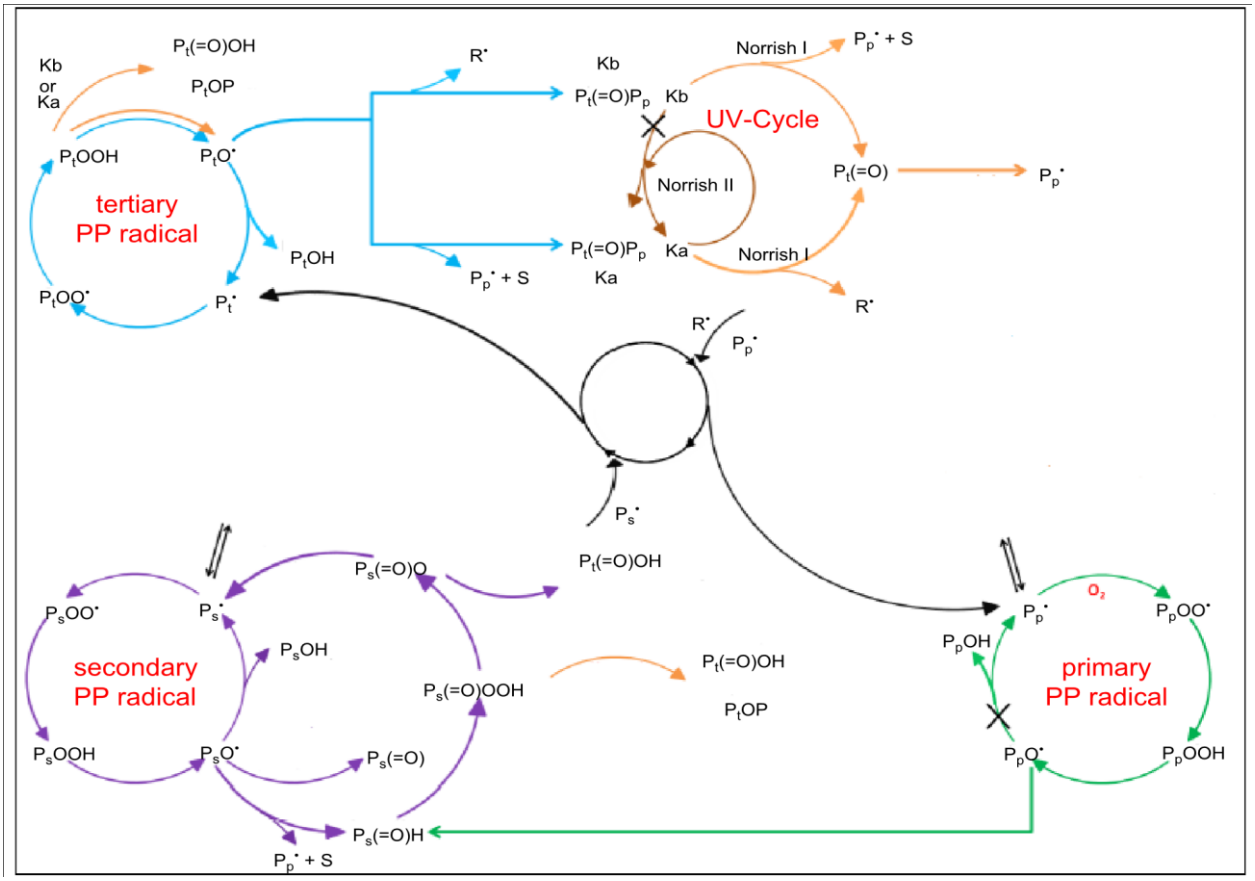
After a review of the qualitative and quantitative aspects of the emissions, and the key trends that determine the profile of the emissions as thermal, temporal, oxidation i.e. availability of oxygen, and nature of the stabilisation packages changes, it is important to contextualise the findings with reference to the contemporary research on thermo-oxidative degradation PP. The important aspects that are considered at this point include:

- the chemical mechanisms for the formation of the major groups of emissions and the key compounds (as regarded in the literature) detected during the current study
- relation of the emission profiles with the macromolecular chemistry and kinetics of thermo-oxidative degradation phenomenon.
- relation between the nature and quantity of the degradation products and the stabilisation packages used in a particular formulation.

In PP, thermo-oxidative degradation begins with the formation of alkyl radicals after the abstraction of hydrogen atoms from vulnerable points along the polymeric chain. A PP chain is made of three types of carbon atoms i.e. primary/methyl groups, secondary/methylene groups and tertiary/methane groups. The presence of the multiple reaction sites in PP appears to complicate the thermo-oxidative degradation in the polymer, in literature the issue in general is circumvented by adopting the so-called general notion of 'the predominant role of the tertiary alky radicals in PP degradation'. The notion implies that the relative differences among the reactivity and the stability of the primary, secondary and the tertiary free radicals formed by the polymer are so significant that the major part of degradation chemistry can be explained only on the basis of the tertiary radicals. The generally accepted order for the relative stabilities of the alkyl radicals is that a tertiary > secondary > primary. Although, widely acclaimed and at the basis of the majority of the literature on PP degradation chemistry, the idea of predominance of tertiary carbon chemistry is still a part of debate in contemporary research. Francoise et al. in their recent work, for example, addressed this issue and proposed methylene groups playing an important role PP degradation. This aspect of PP degradation requires to be reconsidered in the relevant kinetic and mechanistic considerations [3]. The argument is also supported by the role of the primary and secondary alkyl radicals in the genesis of CO and CO_2 during PP degradation [51]. It is therefore, preferred to start the current discussion with the assumption that all three carbons, although to variable extent, do contribute to thermo-oxidative degradation chemistry of

PP, and that ruling out their potential role is only an oversimplification insufficient to explain the degradation completely.

To begin with such an apparently ideal scenario, the three types of carbons atoms along a PP chain i.e. primary, secondary and tertiary, are assumed to generate three types of alkyl radicals each of which, after multiple oxidation reactions, forms corresponding alkoxy and peroxy radicals, and hydroperoxides. The chemistry that follows is succinctly summarised in the so-called closed-loop mechanistic scheme (CLMS) in the Figure: 3.2).



Scheme: 6.2. Closed-Loop Mechanistic scheme of PP degradation [39].

Although, based on the idea of critical pathways, the scheme only takes the key reactions into account, it is still believed to encompass the degradation chemistry of the major groups of PP oxidation i.e. ketones, aldehydes, acids, esters, and alcohols. In CLMS, the oxidation that begins at each of the three types of the alkyl free radicals is formulated into individual loops dedicated to each of the three alkyl radicals. The loops interconnected through isomerization and other reactions form a comprehensive picture of the role of each of the reaction sites along the PP

chain. Each of the three loops has a core comprising of auto-acceleratory oxidation and scission reactions pathways. While alcohols are reported to be the end-product of the loops, there are also various auxiliary pathways protruding-off the core of each loop (Scheme: 6.2). The so-called auxiliary pathways bestow uniqueness to the chemistry of each of the three types of the free radicals. For example:

- The secondary and the tertiary free radical oxidation pathways generate ketones and carboxylic acids, while the former is also known for the formation of α-methylated carboxylic acids.
- Similarly, the aldehydes formed during PP degradation, are an important oxidation product of PP degradation pathways originate from primary and secondary alkyl radicals.
- The only the pathways that are unique to the loop corresponding to the tertiary alkyls radicals, are the ester forming pathways.
- Originally developed for thermo-oxidative degradation in PP, the CLMS has recently been adopted to account for photo-oxidative degradation in the polymer as well. The basic framework of the thermo-oxidative and photo-oxidative degradation versions of the CLMS are mostly the same except that the latter has Norrish reactions to account for photochemistry aspects.

The emissions data acquired during the current study was as diverse as the experimental conditions i.e. thermal and temporal conditions as well availability of oxygen, and the physiochemical features of the samples i.e. the stabilisation packages and physical state etc. Still there are some features that can be ascribed to the results in general. The alcohols, for example, that have been shown to form the core of the loops for the alkyl radicals in the CLMS, were consistently the least, indeed, a negligible part of the emissions across all PP samples. None of the IR spectra showed any peaks corresponding to alcohols. Does that mean that the so-called core of the loops is dismantled by scavenging of the secondary and tertiary alkyl radicals and the subsequently formed –oxy radicals in the stabilised PP ? Since the CLMS is derived for un-stabilised PP, it does not necessarily takes the stabilisation effect into account. Before this question could be answered however, there are multiple other features and limitation of the experimental set-up and PP degradation chemistry that need to be reconsidered.

Alcohols represent the end products of the CLMS for the primary, secondary and tertiary alkyl free radicals in thermo-oxidative degradation of PP. The alcohols are mainly formed by uni-

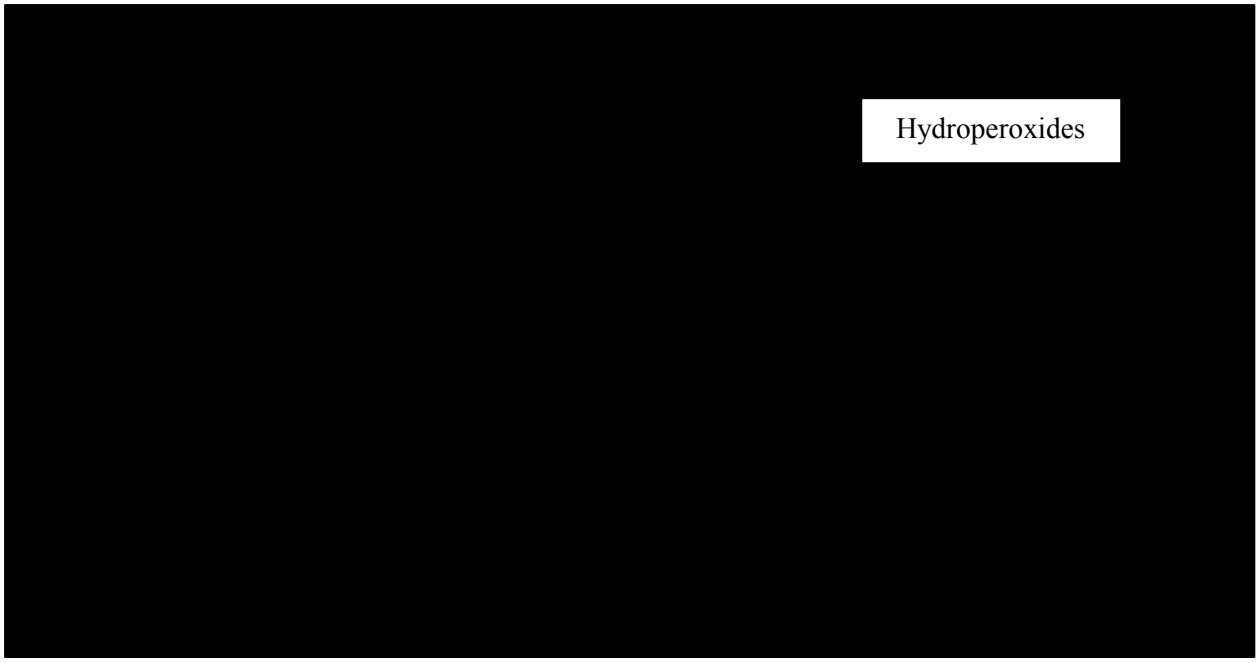
molecular decomposition of hydroperoxides [3, 20, 38, 60, 62]. In uni-molecular decomposition, a hydroperoxides breaks into alkoxy and hydroxide radicals (Scheme: 1.5). The alkoxy thus formed is very reactive and converts into an alcohols after hydrogen abstraction from the polymeric chain. The homolytic splitting of hydroperoxides is promoted primarily by thermal or UV energy, structural defects, e.g. unsaturation, being the secondary features that can enhance the splitting. Although the homolytic splitting had been the predominant explanation of hydroperoxides in a substantial number of early studies on thermo-oxidative degradation in polyolefin, in the wake of experimental findings, it was eventually rejected in the favour of heterolytic/bi-molecular reaction decomposition pathway [39-42]. It is this aspect of PP degradation that need to be considered for mechanistic and kinetic explanations dealing with thermo-oxidative degradation of PP, e.g. CLMS. Provided the common existence of the alcohols in the studies on degradation of polyolefins, if the mechanistic debate behind the formation of alcohols is ignored for a while, the alcohol formation if occurring at all is also in competition with other reactions. One such example is the formation of ketones. A relatively higher emission of the ketones can be regarded as preference of the oxidation chemistry for ketones as compared to the alcohols. Further, the alcohols get oxidised into ketones. The persistently low proportion of the ketones among the PP headspace emissions in the current study renders the above possibilities less relevant.

Another important factors that requires due attention is the existence of the so-called secondary reaction during PP degradation. A PP matrix is not necessarily a non-polar solvent. At any stage in its life cycle, a range of polar functionalities, e.g. aldehydes, acids, ketones and esters as well as the degradation products of antioxidants (in the case of stabilised PP) can potentially be promoting reactions of secondary nature (Scheme: 3.50). Although, the continuous sweeping and trapping of the emissions from sample headspace can be claimed to have significantly reduced the chances of secondary reactions among the primary degradation products of the polymer, the possibility cannot be completely ruled out.

The CLMS is based on the assumption of uni-molecular decomposition of hydroperoxides. Although the idea of uni-molecular decomposition makes the corresponding kinetic scheme simpler, it is not the established mode of hydroperoxides decomposition for PP thermo-oxidative degradation anymore. For thermo-oxidative degradation, especially in the solid-state

of polyolefin, the scheme needs to be revised in the wake of bi-molecular degradation chemistry of hydroperoxides.

Another important features of the oxidation products of PP, as observed in the current study, is the prevalence of aldehydes in the headspace of most of the PP samples. Although effectively controlled by stabilisation packages, e.g. the formulations C (SN1680 + Ga-80), G (SN1680 + GA-80 + SN4120) and O (SN1680 + SL1190 DSTDP), the aldehydes were among the most abundant compounds among the oxidation produsct of PP in many of the formulations. In some formulations, e.g. E and F, the aldehyde formation was detected at as low temperature as 90°C and as early as 2 hrs of ageing. Provided they are not generated by any non-polymeric parts of the stabilised PP formulations, the prevalence of aldehydes among the emissions from PP implies the predominant existence of primary and secondary alkyl radicals. For PP, such an assumption is in disagreement with the popular idea of the so-called tertiary carbon chemistry.



Scheme: 6.3: Key functionalities generated during thermo-oxidative degradation of PP [38].

In literature, one of the commonly reported mechanisms for the formation of aldehyde is through the formation of an intermolecular tetraoxide complex between secondary and tertiary alkoxy radicals that breaks into ketones and aldehydes. The same mechanism has been considered for the chmiluminescence emissions from polyolefin during thermo-oxidative degradation [45]. Based on the assumption of methylene carbon being the origin of the oxidation pathway leading

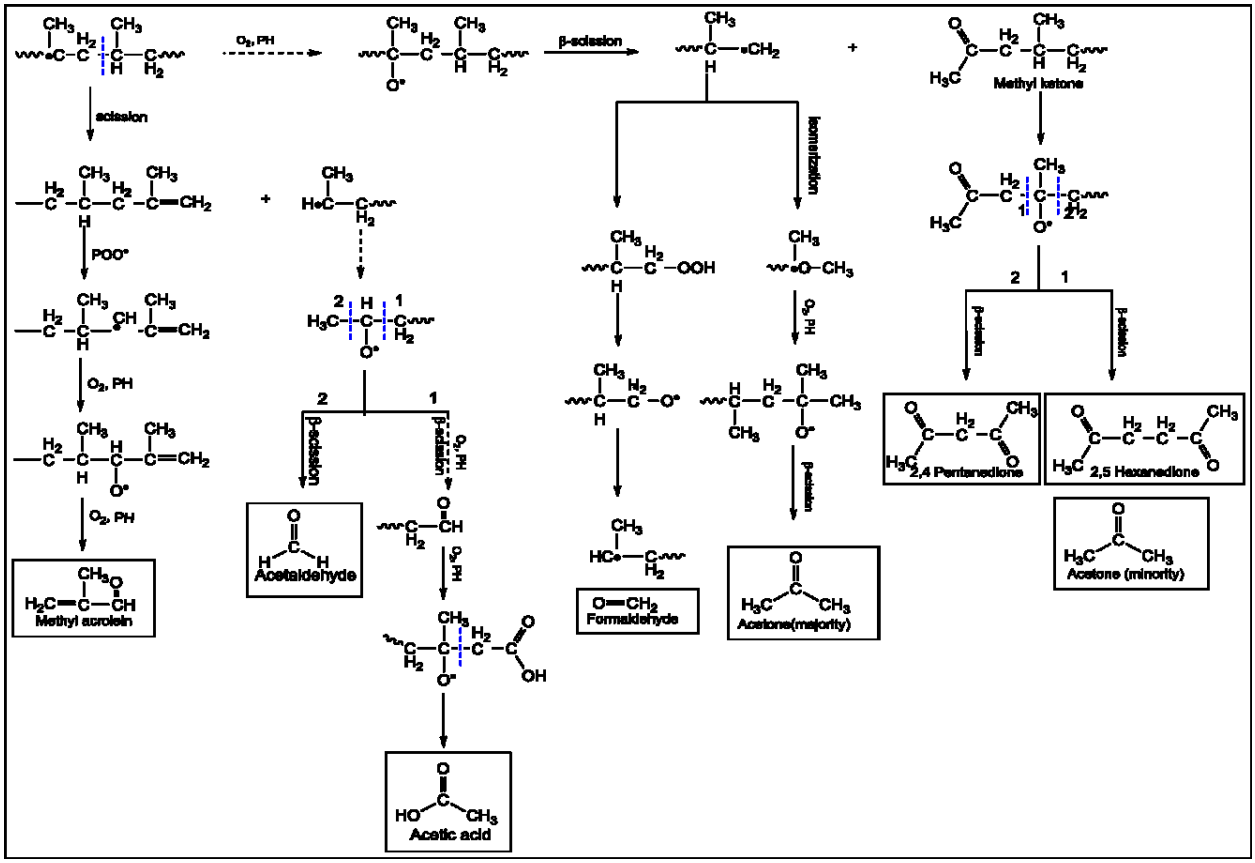
to the formation of aldehydes the minor role of methylene group in the thermo-oxidative degradation chemistry becomes predominant after stabilisation of PP. An alternative explanation is the preferred disposition of the antioxidants to scavenge the tertiary radicals leaving a relatively higher population of the methylene radicals propagating oxidation chemistry leading to aldehyde formation.

Since the PP formulations analysed in the current study were not free of stabilisers, the role of the stabilisers/additives as a potential source of aldehydes cannot be ruled out. The argument also gets support from the thermo-oxidative degradation of the thioesters and calcium stearate that tend to oxidise generating extensive carbonyl emissions when exposed to 150°C in presence of air (Table: 6.16 and Figure: 8.3-8.4). It possibility however, cannot be assured until further work is done to confirm that assumption, e.g. use of isotopically labelled CaSt or by testing the additives in more detail through further combinations.

The mechanistic explanations dedicated to the formation of aldehydes in PP is limited. The aldehydes are generally considered too unstable to exist inside the PP matrix in a substantial yield at a particular time. Their role in PP degradation chemistry has mainly been confined to discussions on to photo-oxidative. In thermo-oxidative degradation it has mainly been treated as the intermediate forming secondary products, e.g. peracids, acids, and lactones, etc. In the current study, the formulations that exhibited higher aldehyde emissions also generated significantly higher acidic emissions, e.g. the formulation H and I, supporting their role reported in literature. In the wake of the considerably higher emissions of aldehydes observed in the current study, it is important that the mechanistic and kinetic formulations behind their formation are revisited.

As one reviews the literature on the emissions from PP it does not take long to see that a major part of the studies that focus on polyolefin emissions tend to stick with a rather limited number of compounds. Acetone, acetic acid, formaldehyde and acetaldehyde, and diketones, for example, are reported in multiple studies. In a recent study, a so-called universal mechanistic scheme encompassing the chemistry behind the genesis of the key volatiles generated by PP has been proposed (Figure: 6.4). In this scheme the established mechanisms that entail the formation of methyl acrolein, acetaldehyde, formaldehyde, acetone, acetic acid, 2, 4-pentanedione, and 2, 5-hexanedione, are explained. The so-called key volatiles (with the

exception of formaldehyde and acetaldehyde) were detected with the method adopted for the current study. None of them however was detected below 150°C. Even at 150°C a major part of the formulations demonstrated a good control over the emissions reducing them to a negligible level. The formulations that mainly did exhibit the presence of the methyl acrolein, acetaldehyde, formaldehyde, acetone, acetic acid, 2, 4-pentanedione, and 2, 5-hexanedione contained hindered phenols, and thioesters along with the phosphite SN1680 for PP stabilisation. Replacing SN1680 with hydroxylamine (FS042) reduced the emission of the key volatile even further. Hence, it will not be wrong to say that most of the key volatiles that are associated with thermo-oxidative degradation of PP have been effectively controlled by most of the stabilisation packages.



Scheme: 6.4. Key carbonyls formed during thermo-oxidative degradation of PP [59].

Another important point is that all reactions in the so-called universal scheme for the key volatiles of PP degradation begin with a tertiary alkyl radical, ignoring any possible contributions by the secondary and primary alkyl and alkoxy radicals. The tertiary free radicals in the scheme have been reported to undergoe multiple oxidation and scission pathways ending with different end-products. The controlled formation of the end products thus infers the

radicals being sufficiently scavenged by most of the stabilisation packages used in the current study [52]. This interpretation again tends to limit the implications of the popular works on the PP emissions and relevant chemistry, rather limited for the polymer in its stabilised form. At the same time, it compels one to review the stabilisers for potential selectivity in scavenging the free radicals based on their stereochemistry and structural orientations.

6.1.2. Analysis of the emissions by MSSV-GC-MS

All fifteen polymeric formulations initially analysed by SPME-GC-MS have also been analysed by MSSV-GC-MS for the emissions. In the MSSV-GC-MS analysis thermo-oxidative degradation was conducted in a sealed micro-glass tube where the polymeric sample was allowed to age at 150°C for a period of 20 hrs. Since the sealed micro glass tubes had limited availability of oxygen, a difference in the emissions, as expected, in comparison with the emissions generated in the continuous availability of air during SPME-GC-MS analysis was observed. The difference among the emissions from the same sample when measured by MSSV-GC-MS and SPME-GC-MS is shown in the Figure: 6.10 and 6.11. The two chromatograms in each of the two Figures represent headspace emissions from the formulation B (SN1680 + SN1010). The Figure: 6.10 shows the lower part of the chromatograms, while the Figure: 6.11 shows the high boilers in the same pair of the chromatograms. The key observations between the chromatograms acquired by the two methods are as follows:

- The total emissions for the MSSV-GC-MS methods was significantly less than the SPME-GCMS analysis.
- The emission measured by MSSV-GC-MS contained higher unsaturated hydrocarbons, which can be associated with low oxygen availability for PP degradation (Figure: 6.10-6.11).
- Comparatively higher carbonyl contents, e.g. ketones and aldehydes were observed in the emissions analysed by SPME-GC-MS (Figure: 6.10-6.11).
- A greater range of antioxidant-based degradation products was detected in the sample headspace analysed by MSSV-GC-MS in comparison with SPME-GC-MS (Figure: 6.11).

The variation in the relative ratio of the hydrocarbons and carbonyl content for the formulation B, when analysed by the two methods can be attributed to difference in the oxygen available for thermo-oxidative degradation. The comparatively lower range of the antioxidants based degradation products detected in the SPME-GC-MS trace can be due to their selective adsorption by the SPME fibre coating. MSSV extraction, in this regard, has an advantage over

SPME-GC-MS analysis of the emissions. The technique however, need to be optimised further, especially for factors like undesired degradation of the polymer inside the GC inlet. Further, the chances of secondary reactions among the degradation become more likely inside the limited space of a sealed micro glass used for headspace sampling.

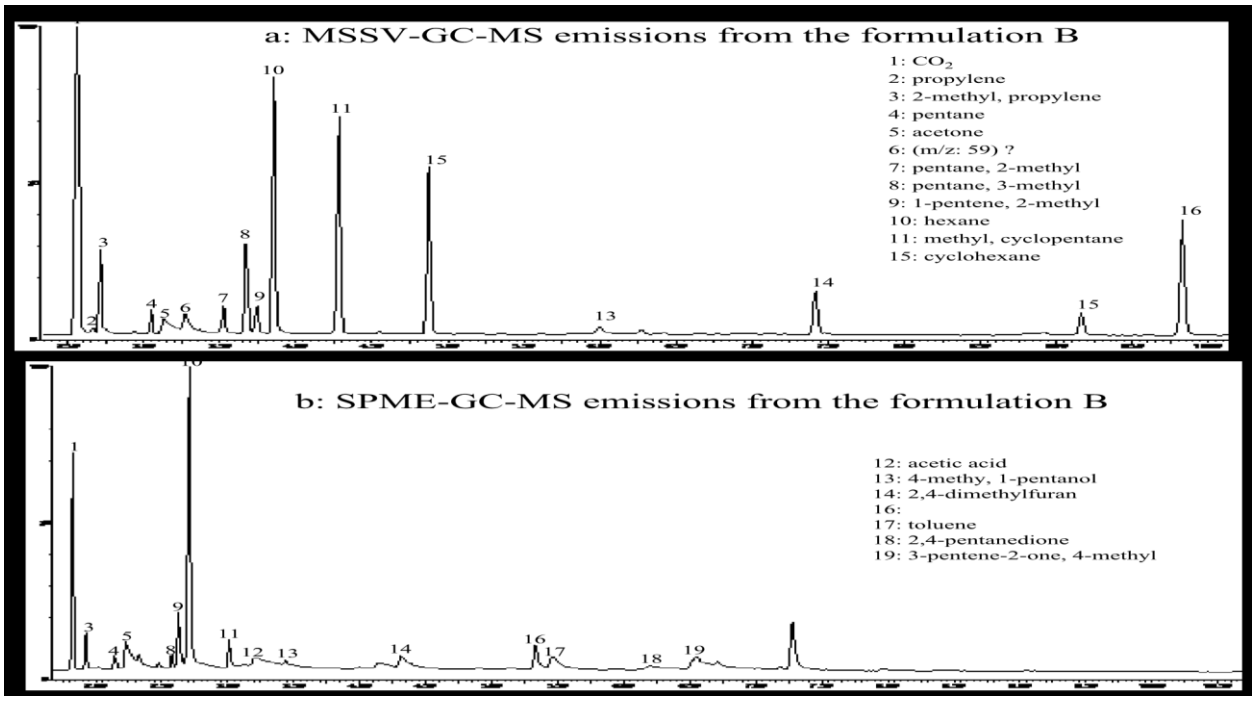


Figure: 6.10. MSSV-GC-MS trace of the formulation B.

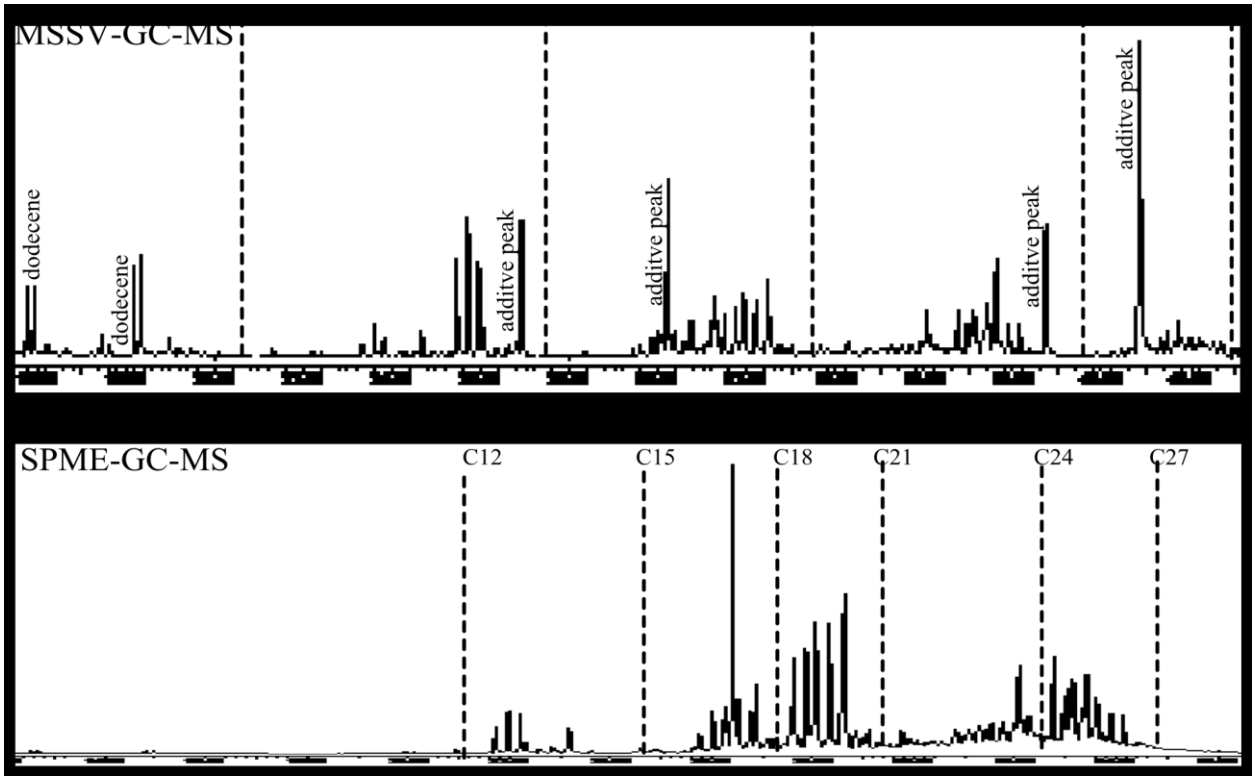


Figure: 6.11. MSSV-GC-MS and SPME-GC-MS traces of the formulations B.

6.1.3. Degradation products of the additives/antioxidants

Stabilisation of polyolefin is determined as much by physical properties of the antioxidants as by their chemical structure and reactivity. The antioxidants are exposed to severe conditions, e.g. high processing temperature, during which they are likely to undergo thermal and oxidative degradation, subsequently breaking down into various secondary structures. The degradation and transformation products thus formed, in many cases, possess antioxidant properties that significantly contribute to the overall stabilisation action of the parent antioxidant structure. Mainly polar in nature, the small volatile structures formed by degradation of the antioxidants are prone to escape the non-polar PP matrix. Their emission can result in depletion of active concentration and hence the stabilisation that can be expected from the initial concentration of the antioxidant. The antioxidant degradation and emission of the fragments is also important due to their effect on the aesthetic properties of a polymer, especially in the applications where the aesthetics, e.g. smell and colour, are the part of material specification criteria, e.g. automobile interiors. A good understanding of the physiochemical of the antioxidant degradation products, therefore, is an important part of research on polymer stabilisation chemistry. In the current study, a range of antioxidants were analysed for their degradation and the subsequent emissions from them. They were analysed under multiple degradation conditions and tested as a part of the PP matrix as well as at their own. The identification of the antioxidants degradation products was done based on the:

- Theoretical knowledge of the composition of the PP samples
- Comparison of the polymer headspace emission with that of the emission from the stabilisers tested at their own
- Comparison with Mass spectral libraries of MS databases, and comparison with reference material, available for a number of compounds detected in the samples.

Although a wide range of structures were detected as the degradation products of the antioxidants, not all of them are reported in here (Table: 6.16-6.17 and Figure: 6.12-6.16). Some of the compounds, although detected, are not reported as they could not be identified with sufficient authenticity, while others could not be included due to secrecy agreement with the sponsor of the research project.

A significant proportion of the compounds detected can be associated with potential antioxidant character. The structure: I, II, III, IV, IX, XI, XV and XIX in the Figure: 6.16, for example are

phenolic have phenolic groups. Substituted with alkyl groups, they are potential hindered phenols of smaller molecular weight. Some compounds on the other hand, e.g. the oxidation products of CaSt and thioesters that include aldehydes, ketones and esters, can interact with the degradation products in the polymeric matrix leading to secondary reaction and hence promoting further degradation of the polymer. As mentioned earlier, the antioxidants were tested for their degradation at their own as well as a part of the PP matrix. The temporal and thermal increase resulted in an increase in the degradation and subsequent emissions from the antioxidants, both at their own as well as when inside the PP matrix.

Under the same experimental conditions, the degradation of an antioxidant while inside the PP matrix was significantly reduced in comparison with its degradation at its own (See the Table: 6.17 and Figure: 6.12-6.13). Similarly the effect of the co-stabilisers in a stabilisation packages in a PP formulation was also evident and rather interesting. Calcium stearate and DSTDP, for example, when aged individually degraded extensively generating a range of carbonyl emissions. Incorporating the two compounds into PP matrix however, reduced the emissions to a very low level. Further, the low antioxidant-based emissions were in a good relationship with the low PP emissions and good stability of a formulation. Such effect varied among the formulations as the composition of the stabilisation packages changed. A consistently higher emission of degradation products, theoretically characteristic of the chemical structure of CaSt, for example, were observed when the antacid was used with F042. Similarly, the carbonyl emissions of DSTDP, were reduced when the antioxidant was used in combination with SN1010. In some example, the emissions from the formulations were not detected in the chromatograms of the antioxidants tested at their own, suggesting them as the products of mutual interaction among the stabilisation components of a multicomponent stabilisation package in a given PP formulation.

- The hindered phenols and phosphite generated a range of degradation products of aromatic nature (Figure: 6.12 and 6.13). When the same antioxidants were tested as a part of the PP formulations (in combinations with the other stabilisers as mentioned in the Table: 2.3-2.5 of the Chapter: 2), the hindered phenols and the phosphite antioxidant i.e. SN1680, reproduced majority of the degradation products that were detected din their headspace when tested separately. It was easier to differentiate the degradation products of the hindered phenols and

phosphites from those of the rest of the antioxidants and those of the polymer, due to their aromatic structures.

The degradation of the two hindered phenols i.e. SN1010 and GA-80 showed the latter more thermally stable during the first 4 hrs of ageing. Although GA-80 showed a significant increase in its degradation over-time, the degradation products were not reproduced among the emissions from the formulation containing the antioxidant GA-80 as a part of their stabilisation systems, while SN1010 based degradation was continuously higher even inside the PP matrix.
The degradation products of SN1010 have potential antioxidant character; loss of such species through evaporation can be associated with the apparent lower stabilisation of the antioxidant observed in the CL analysis and general emissions trends of the formulations that contained the antioxidant. Further, greater degradation of PP at higher temperature also need to be considered in the context of higher degradation of the antioxidants and their subsequent loss through evaporation with increase in heating time and temperature.

- The emissions from the thioesters i.e. SN4120 and DSTDP (Figure: 6.14), were mainly carbonyl compounds i.e. aldehydes, ketones, esters and organic acids. The identification of the degradation products of the thioesters as a part of the PP formulations was difficult due to the possibility of the polymer itself oxidising/degrading into similar series of compounds, e.g. acids, aldehydes, ketones and hydrocarbons etc.
- Calcium stearate, an antacids, degraded profusely generating a wide range of carbonyl compounds (Table: 6.16 and Figure: 10.4). Although the similar compounds were observed in the headspace of the PP formulations containing CaSt, their relative proportion, especially the carbonyls, was significantly less.
- SL1190, a light stabilisers, showed a good stability during 20 hrs of exposure to 150°C. The only degradation products that were detected include toluene and xylene (Figure: 6.15 and Table: 6.17).
- Vitamin E, due to its low thermal stability and low melting/boiling point was not tested for its degradation. It degradation, at very initial stage was a source of serious contamination of the analytical system, and was avoided at this stage.

SN1680, the organo-phosphite used as a processing stabiliser has been analysed for its thermo-oxidative degradation behaviour both at its own and while incorporated in PP matrix along with a range thioesters, hindered phenols and a light stabiliser (Table: 2.3 and 2.5). 2, 6-

bis(1,1dimethylethyl)phenol was observed in the headspace of the antioxidant after thermo-oxidative degradation of the antioxidant for 4 hrs and 20 hrs. The other compounds that were detected include 2-*t*-butyl-phenol, tri-*t*-butyl phenol, and two compounds at the m/z of 244 and 248. The emission of the structure III was continuously observed and significantly increased over time. The same structure was also detected in the headspace of the formulations containing the antioxidant i.e. SN1680.

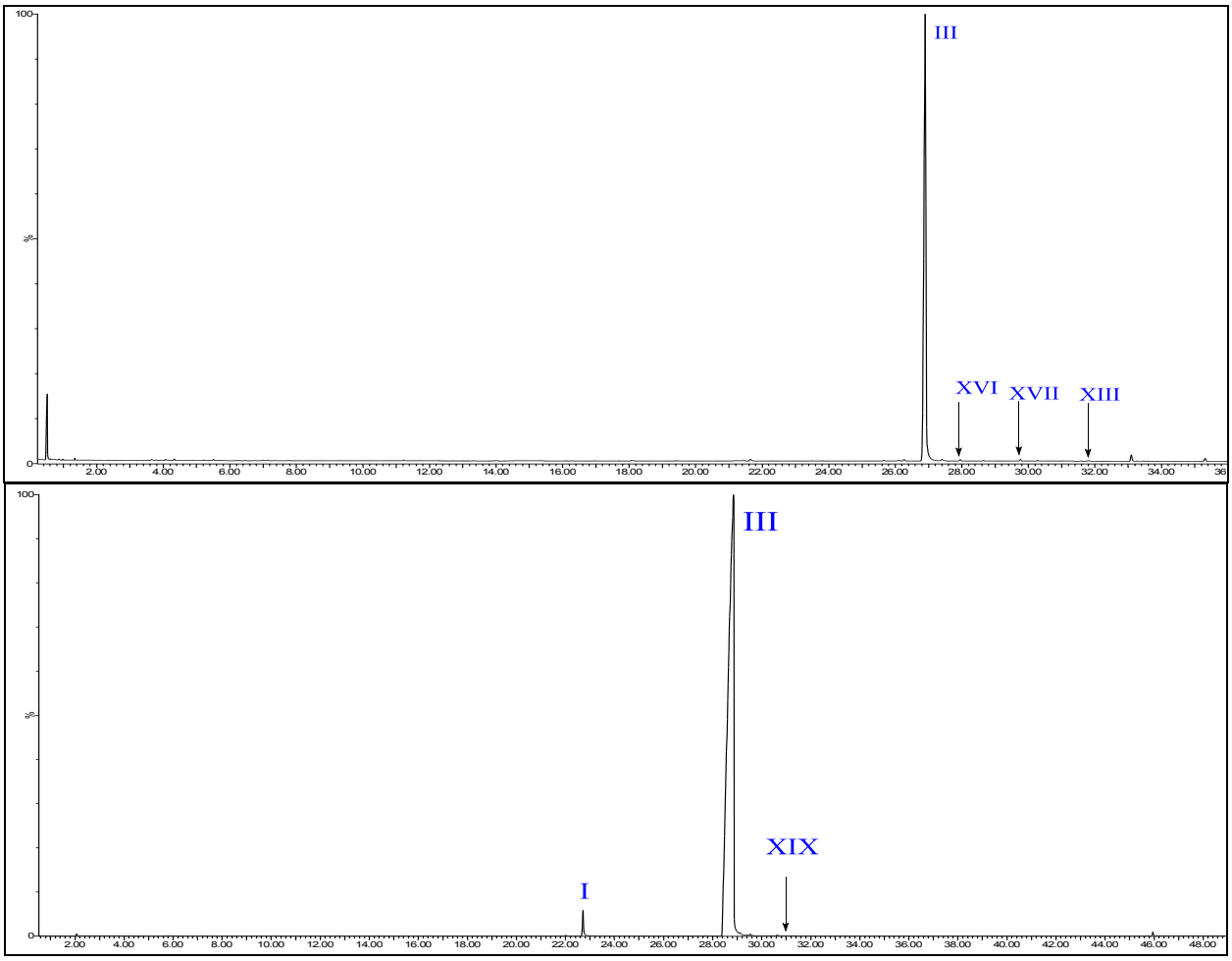


Figure: 6.12. GC-MS traces of the emissions from the SN1680.

Unlike hindered phenols the thioesters i.e. DSTDP and SN4120, as expected from their structure, emitted on-aromatic carbonyl groups. DSTDP emitted ketones, aldehydes, asters and acids, while the SN4120 emitted aldehydes, predominantly. The carbonyl-based emissions of the thioesters were manipulated differently when they were present as a part of stabilisation packages for PP. The effect cannot be more pronounced than in the formulation D verses F and the formulation C verses E. In the first pair, the carbonyl emissions expected for DSTDP are reduced to a comparatively very low level in presence of SN1010, replacing the hindered

phenols with GA-80 (another hindered phenol) led to a substantial increase in the carbonyl emissions from the formulation.

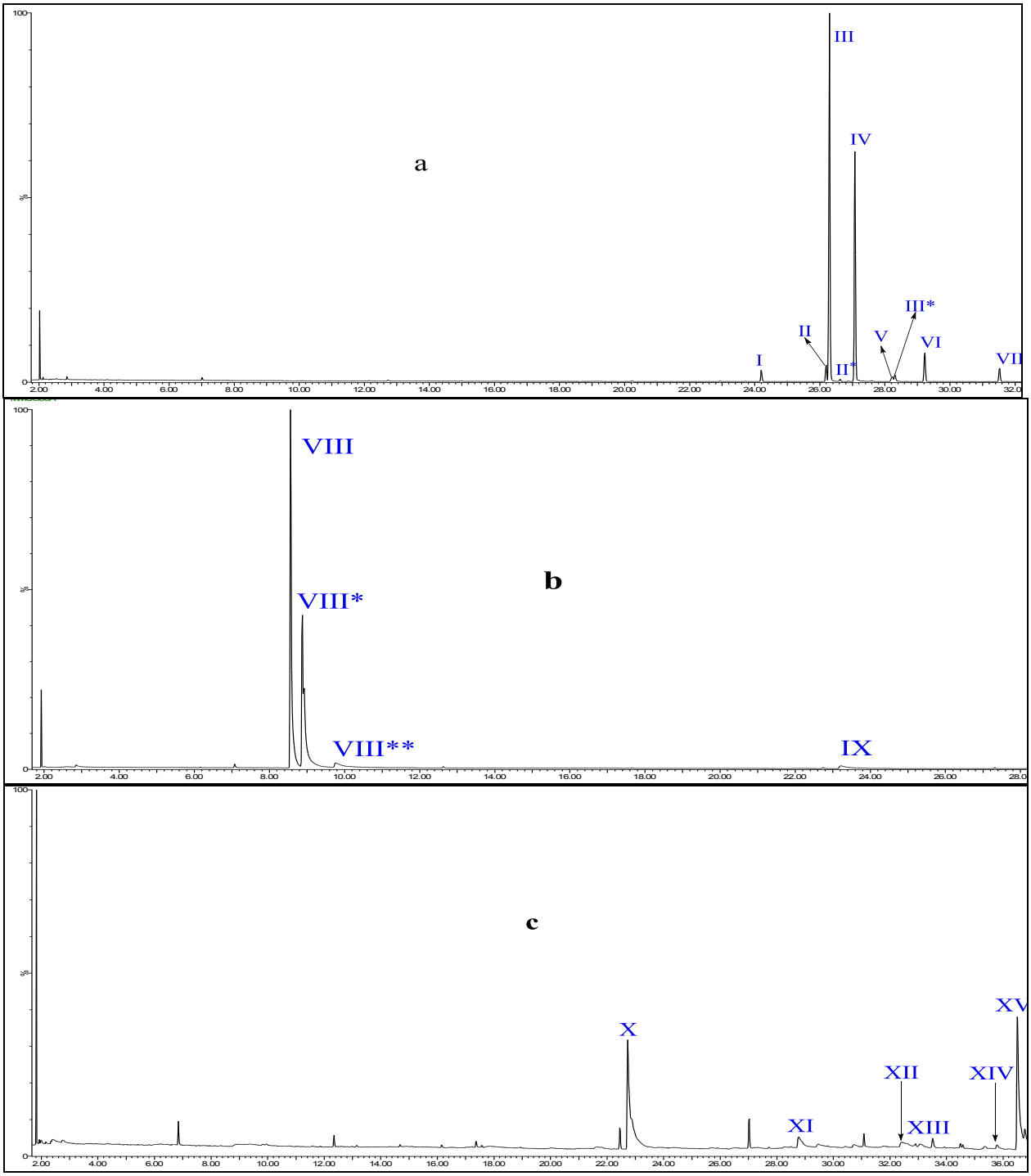


Figure: 6.13. GC-MS trace of thermal degradation products of SN1010 aged at 150°C for 4hrs and GA-80 aged at 150°C for 4hrs (b) and 20hrs (c) in presence of air.

A similar response can be attributed to CaSt, the salt used as an ant-acid in PP. The role of the salts like CaSt have been discussed in literature as the extrinsic agents that can affect the

initiation stages of polyolefin degradation. The affect varies i.e. it can be promoting inhibiting degradation of the polymer depending on the chemical nature of the salt, it concentration and the external conditions a polymer is exposed to, e.g. it has been found pro-degrading in solution state and anti-degrading in the solid polymeric formulations at moderate ageing temperature i.e. 50°C. The role of the concentration, reported to be a key factor to determine the nature of the affect a salt can have on oxidative degradation of a polymer, also doe need to be considered.

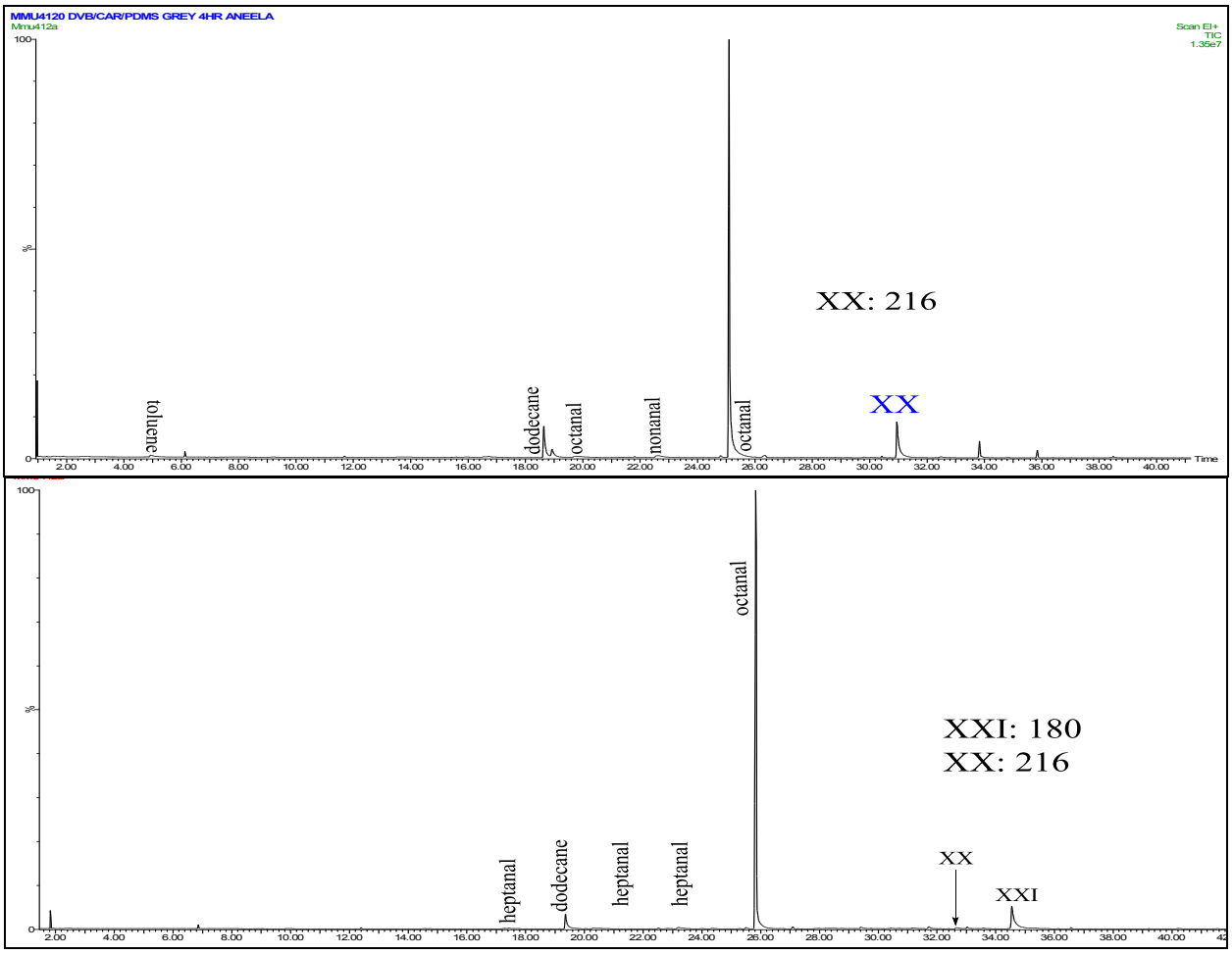


Figure: 6.14. GC-MS trace of thermal degradation products of SN4120.

For the current study, CaSt was a part of the stabilisation packages of all PP formulations (the formulation M being the only exception where the additive was replaced by ZnO) that were investigated. Exposed to thermo-oxidative degradation at 150°C, CaSt degraded profusely generating a range of carbonyl compounds in its headspace (Table: 6.16). Although, inside a PP matrix the salt is shielded from the heat and oxygen contact to a significant extent, but is that affect enough to neglect the possibility of its thermo-oxidative degradation and impact of the

subsequently formed oxidation products on the chemistry of thermo-oxidative degradation and degradation of the polymer in general? This apparently simple question becomes more complicated after the review of the relative carbonyl portion of the emissions from various formulations.

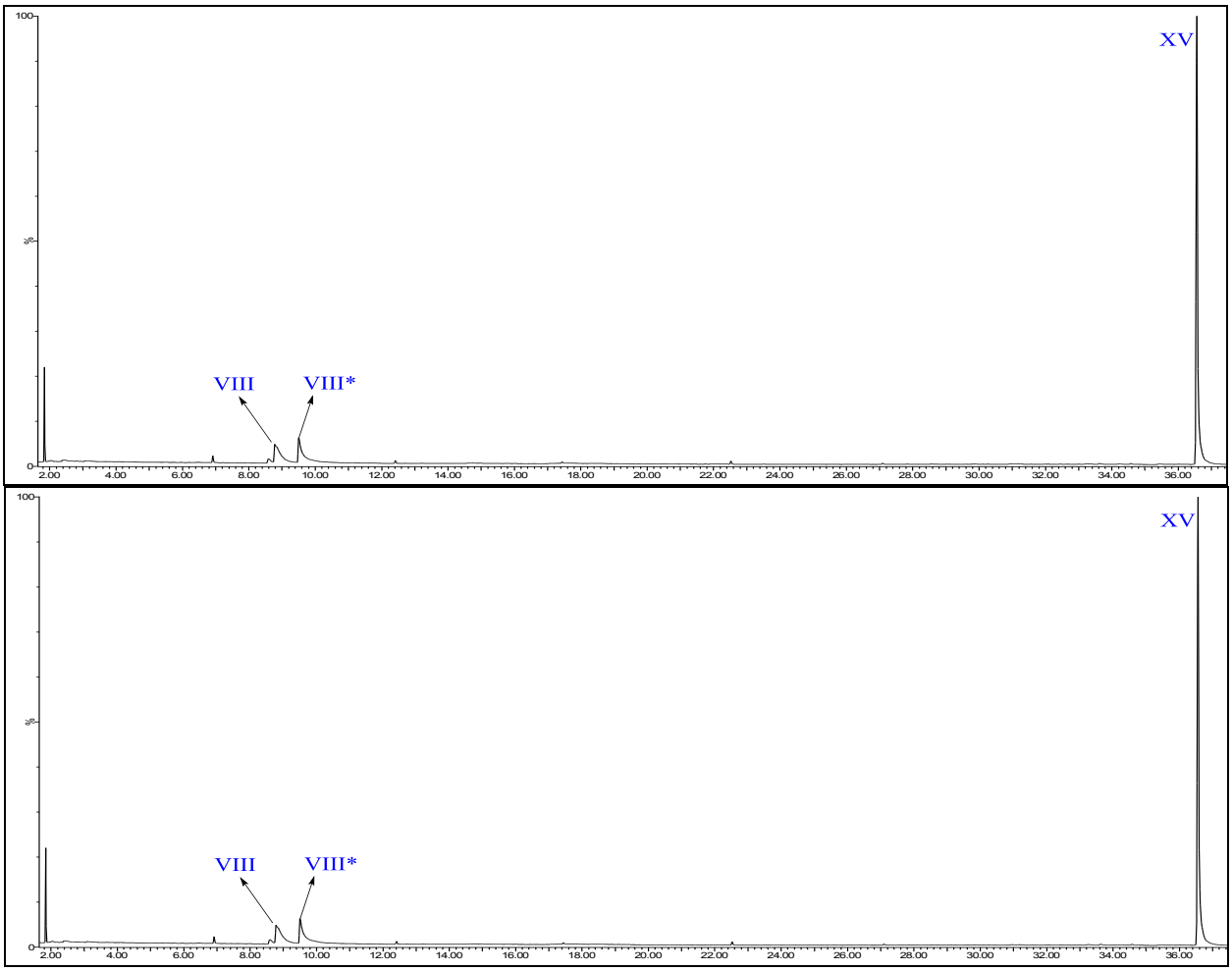


Figure: 6.15. GC-MS trace of emissions from SL1190.

In the group: 1 formulations (Table: 2.3), for example, the formulation B, C and G, showed a very negligible carbonyl based emission, while the emissions from the formulation D, E and F were mainly carbonyl-based. On the basis of the degradation behaviour of CaSt, if the antiacid is considered a potential source of the carbonyl based emissions, it certainly is affected by the antioxidants used alongside it in a given polymeric matrix. As for as the Group: 1 formulations are the concerned, they all contained hindered phenols, and phosphite as well as CaSt in them. The key differentiating feature among them was that the formulation B, C and G, showing low carbonyl emissions, contained no thioester (G being the only exception that had SN4120), while the formulation D, E and F had a thioester in them. The thioesters themselves have been

observed to degrade generating carbonyls, preferably aldehydes, when exposed to thermos-oxidative degradation at their own. The presence of the thioesters and the CaSt together in the same formulations therefore, does tend to exacerbate the carbonyl-based emissions made by the corresponding formulations.

In the discussions on the chemistry of the pro and anti-degradant behaviour of metal the latter has been attributed to the formation of metal-hydroperoxide complex. Thioester-based antioxidants are the secondary antioxidants that primarily target hydro-peroxides, their presence in a formulation is likely to affect the metal-hydroperoxide complex formation that can shift the anti-degradant behaviour of CaSt to the lower region of the scale. This assumption however, does need to be tested, before a conclusive statement can be made on the matter. One such attempt was made by replacing CaSt in the formulation N with ZnO. Both thioester and CaSt being removed one expects that the carbonyl emission is controlled significantly if not completely. However, after observing the emission behaviour of the formulation N, it was realised that such response was after-all an overestimation of the stabilisation that could be achieved with Vitamin E as the sole stabiliser in a PP matrix. Vitamin E is a naturally existing member of hindered phenols family. It's applications in synthetic systems has previously been limited due to its thermal instability generally required for the antioxidants to survive service and processing conditions of synthetic polymer.

Table: 6.16. Emissions generated during thermo-oxidative degradation of CaSt.

Group	range	relative percent emission
Carbon dioxide		0.42
Hydrocarbons	C10-C18	6.00
Ketones	C3-C15	27.50
Aldehydes	C4-C15	57.00
Acids	C3-C16	2.40
Alcohols	C6-C13	3.25
Un-identified carbonyls		3.30

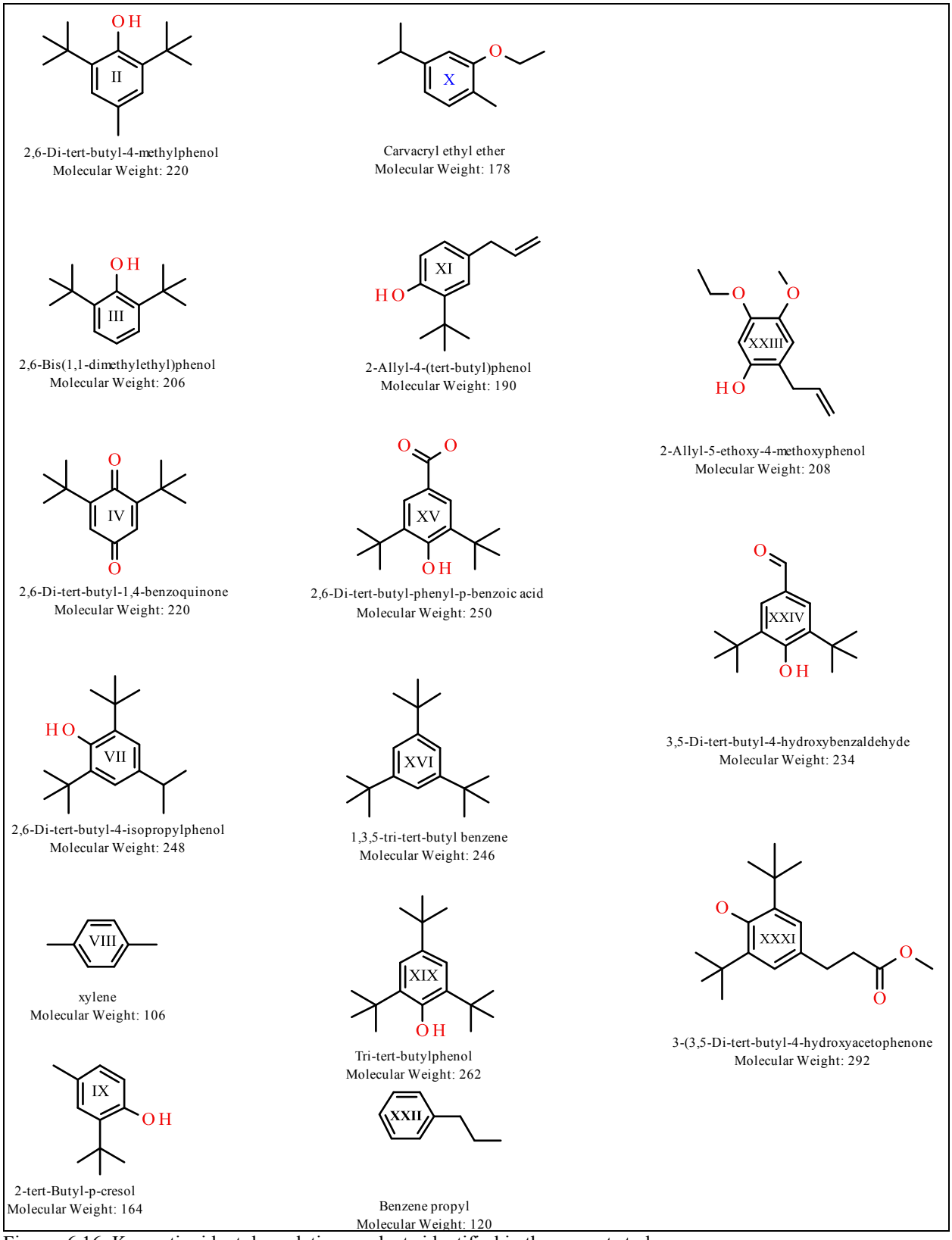


Figure: 6.16. Key antioxidant degradation products identified in the current study.

Table: 6.17. Antioxidant-based degradation products identified in the headspace of the formulation A-G.

			Sample ageing time (hrs)													
			A		B		C		D		E		F		G	
I.D	**m/z**	**Chemical Name**	2	8	2	20	2	20	2	20	2	20	2	20	2	20
II	220	2,6-di-tert-butyl-4-methylphenol	*		*	*								*		
III	206	2,4-di-tert-butylphenol	*	*	*	*	*		*	*	*		*	*	*	*
IV	220	2,6-di-tert-butyl-1,4-benzoquinon			*	*					*		*			
V	168	?			*											
VI	248	2,6-Di-tert-butyl-4-isopropyl phenol														
VII	248	2,6-Di-tert-butyl-4-isopropyl phenol isomer			*											
VIII	106	Xylene														
IX	164	2-tert-butyl-p-cresol														
X	178	Carvacryl ether ether								*						
XI	190	2-Allyl-4-(tert-butyl) phenol														
XII	192	Neopentyl benzoate														
XIII	236	2,6-Di-tert-butyl-4-hydroxymethylphenol	*				*									
XIV	264	?														
XV	250	?														
XVI	246	1,3,5-tri-tert-butylbenzene														
XVII	244	?														
XVIII	248	2,6-Di-tert-butyl-4-isopropyl phenol isomer				*				*						
XIX	262	Tri-tert-butyl-phenol														
XX	216	?														
XXI	180	2-tert-butyl-4-methoxyphenol					*									*
XXII	120	Benzene propyl	*			*							*			
XXIII	208	2-Allyl-5-ethoxy-4-methoxyphenol			*	*				*						
XXIV	234	3,5-di-tert-butyl-4-hydroxybenzaldehyde (isomer of XXIX			*											
XXV	210	?	*													
XXVI	140	?								*						
XXVII	180	2-tert-butyl-4-methoxyphenol				*				*						
XXVIII	232	7,9-di-tert-butyl-1-oxaspirodeca-6,9-diene-2,8-dione				*										
XXIX	234	3,5-di-tert-butyl-4-hydroxybenzaldehyde			*	*				*				*		
XXX	278	3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid														
XXXI	292	3-(3,5-di-tert-butyl-4-hydroxyphenyl) methylpropanoate														

7. CONCLUSIONS AND FURTHER WORK

7.1. Conclusions

The key conclusions that can be drawn from the results and the discussion on the experimental observations are as follows:

- As evident from the method development section of the current report, the analysis of the emissions from a polymeric formulation is significantly affected by the method of analysis, especially the sampling technique. Conventionally adopted methods and so-called material testing standard tests methods, e.g. static headspace and VDA-278, are not necessarily sensitive enough to generate a true picture of the trace level emissions characteristic of stabilised PP. Less commonly used methods, on the other hand, have been demonstrated to generate emission data many folds improved both in the qualitative and quantitative aspects.

- It is also demonstrated that conventionally used IR spectroscopic analysis of thermo-oxidative degradation in solid-state PP formulations generates an under-estimated picture of degradation when compared with the emissions made by the same formulations under same experimental conditions. A significant proportion of the emissions belonging to a range of chemical functionalities start appearing at very early stage during degradation of stabilised PP, and change significantly in response to the factors like ageing time and temperature, composition of stabilisation packages, and variation in the oxygen availability etc. IR analysis of the solid polymeric samples, on the other hand, generates data with limited qualitative and quantitative aspects. It is, therefore, safe to say that provided the mechanisms behind the formation of the compounds detected among the emissions are understood, the PP emissions can provide another window into the chemistry of polymer degradation. In the light of the tremendous emission profiles and apparently less significant changes in the chemistry of polymeric matrix, suggestion that the emissions/low molecular weight products of polymer degradation have previously been underestimated in the discussion on the chemistry and kinetics of the process, will not be too big a claim to make.

- It is observed that PP, even in its adequately stabilised form, emits a range of compounds including hydrocarbons, carbonyls and degradation products of the antioxidants used for stabilisation. The temporal, thermal and stabilisation effect, as well as availability of oxygen generates a significant impact on the qualitative as well as quantitative aspects of the emissions

from PP. Although below 150°C the degradation products/emissions from PP were predominantly hydrocarbons. Interesting patterns that were reproducible across the results were observed. A relation between the hydrocarbon emissions and stabilisation packages was evident. In the formulation B, for example, a comparatively higher content of unsaturated hydrocarbons was observed. In presence of hydroxylamine, the hydrocarbons, in general, were reduced 10-20% in comparison with the formulations containing SN1680 used as the processing stabiliser. The existence of extensive isomerism observed for the hydrocarbons, although unresolved at this stage, can be important to provide an insight into PP chain scission. Increasing the ageing temperature to 150°C changed the degradation of PP to oxidative pathways. As the ageing temperature reached 150°C, the polymer was observed to produce a substantial amount of oxidation products as well as hydrocarbons. The differences among the stabilisation packages in controlling the emissions and over-all degradation were also more pronounced at 150°C.

- At low temperature i.e. 90°C and 120°C, the hindered phenols in presence of phosphite-type antioxidant i.e. SN1680, demonstrated a better control over most of the carbonyls, except ketones. At higher temperature i.e. 150°C, however, the carbonyl emissions became more pronounced; alcohols, acids and esters and ketones were detected. Between the two hindered phenols analysed in the current study i.e. SN1010 and GA-80, the latter demonstrated better PP stabilisation and control over emissions from the polymer. The better stabilisation and less degradation products observed for GA-80 as emissions, can be associated with better thermal stability of the antioxidant and relatively improved physical mobility inside a PP matric, when compared with SN1010.

- The general PP emissions and CL analysis of the polymer showed that the relationship between hindered phenols and thioesters is not a simple synergist type at group level. Rather, it is more selective among the individual compounds from the two families stabilisers. The hindered phenol SN1010, for example, demonstrated synergism when used in combination with DSTDP, while an antagonistic effect was observed for SN4120. More interestingly, the opposite has been observed for GA-80 used in combination with the two thioesters.

- An important conclusion drawn from the general composition of the total emissions across the PP formulations analysed in the current study is that the thermo-oxidative degradation

chemistry is guided more by bi-molecular/heterolytic decomposition of the hydroperoxides inside the PP matrix. An important example in case is the relative proportion of the alcohols and ketones detected among the headspace emissions. The two functionalities represent the main and the by-product of the uni-molecular decomposition of hydroperoxides in PP. Both groups of carbonyls formed a relatively negligible proportion of the total headspace emissions for all formulations, in general. The results are in agreement with the literature supporting bi-molecular decomposition mode for hydroperoxides, and recommend homolytic decomposition of to be revisited before adopting it for mechanistic and kinetic explanations for thermo-oxidative degradation of PP.

- An important feature of PP degradation chemistry is the presence of multiple reaction sites i.e. methyl, methylene and methane, along the polymeric carbon chain. The relative proportion of various functionalities among the PP headspace emissions revealed interesting features about the role of the methyl, methylene and methine carbons in PP. Aldehydes, previously associated mainly with primary alkyl radicals, for example, have been the major part of the emissions in most of the formulations, while ketones that are known as oxidation products of tertiary alkyl radicals predominantly, were reduced to negligible level in most of the formulations. The results can be explained by assuming the tertiary alkyl radicals and associated oxidative pathways being sufficiently scavenged by the antioxidants.

- Carbon dioxide, an important product of thermo-oxidative degradation of polymers, has recently been used to trace oxidation chemistry of PP. In un-stabilised PP, it is reported to result from oxidation pathways that originate at secondary (methylene) and primary alkyl (methyl) radicals in PP, hence supporting the generally under-estimated role of methylene and methyl groups in degradation of PP. In the current study, CO_2 was detected among the emissions from all formulations, which varied in response to the composition of the stabilisation packages in the samples. Further, the relative proportion of the CO_2 emissions also changed with change in degradation conditions i.e. degradation time and temperature etc. In general, the emission decreased with increase in the degradation temperature (Figure: 6.9). Existence of particular trends does support the role of CO_2 in understanding PP degradation chemistry. The CO_2 data however, needs more authenticity through better experimental design.

- A range of oxidation products that form the basis of important mechanistic and kinetic formulations for thermo-oxidative degradation of PP does seem to be less relevant to the behaviour of the polymer in its stabilised form. Acetone, acetic acid, methyl acrolein, 2,4-pentane diketone, and 2,4-hexadiketones, for example, have been efficiently controlled by most of the stabilisation packages used for PP stabilisation in the current study.

- Previously, the antioxidant degradation products in the PP headspace emissions has not been paid much attention. Other than the potential toxicity associated with them, the antioxidant degradation and subsequent emissions are important, as they can cause affect over-all stabilisation efficiency of a stabilisation package by reducing the active concentration of the antioxidants. In the current study, the PP formulations with low stabilisation have consistently been observed to generate high antioxidant-based emissions. The observed low stabilisation can, in part, be attributed to the loss of the stabilisers as degradation products in the headspace emissions. A significant proportion of antioxidant emissions, especially those associated with the phosphite-type and hindered phenol antioxidant groups, were the compounds with potential antioxidant character.

- Primarily determined by their thermally labile nature, the antioxidant-based emissions from a particular antioxidant significantly changed significantly with any change in the composition of the stabilisation packages. SN1010, for example, showed an increase in emission of its degradation products when used with a thioester.

- A review of the PP emissions in the context of the multiple reactive sites in the polymer chain revealed a slightly different aspect of PP degradation. The data interpretations for the current study appeared more complex than the explanations generally adopted in majority of the mechanistic and kinetic formulation of PP degradation. Formation of various important functionalities during PP degradation, is reported to be specific in their point of origin along the PP chain. Ketones, for example, are consistently associated with the tertiary alkyl and alkoxy radicals, while the primary radicals have been reported to quickly stabilise themselves into aldehydes. Variation in the relative proportion of the two groups among the emissions from formulations with different stabilisation packages was evident. It is inferred that stabilisation changed the role of the various types of the free radicals in degradation process, hence affecting the relative ratio of the subsequently formed carbonyls. Low ketone emissions in most of the

formulations, for example, show an average stabilisation package capable of scavenging the tertiary radicals significantly, while the high aldehydes in some of the formulations reveal the predominant role of the primary free radicals in PP degradation.

- The argument that stabilisation significantly alters degradation chemistry is also supported by the fact that a range of degradation products that have been reported and widely discussed among the PP headspace emissions, e.g. acetic acid, methyl acrolein, and acetone, were only the minority or too negligible to be detected in most of the formulations investigated in the current study. A more accurate identification of the emissions and the identification of their source in a polymeric matrix, however is very important and can be conducted by using isotopically labelled stabilisers (suggested in the recommendations for the further work on the subject) [59, 123].

7.2. Further work

7.2.1. New formulations

The current study has shown that stabilisers can significantly affect the chemical nature and the relative proportion of various types of low molecular weight degradation products/emissions. Further, the emissions from the stabilised PP formulations are significantly different from the emissions generally reported for the polymer in its un-stabilised form. Hence, the assumption that the polymer emissions bear a link with the underlying chemistry of polymer degradation is strengthened. The area however, is only partly investigated, and lacks in experimental data. It also need to be explored with reference to the range of the factors affecting PP degradation, e.g. PP processing parameters etc.

Although, interesting trends have been observed during the current study, it has also been realised that for a more comprehensive and systematic approach on the subject, there still is a range of stabilisation packages that need to be analysed. Based on the results of the current study, eight different formulations with different stabilisation packages, are proposed (Table: 7.1) as further works continuation. The formulations are assumed to fill the gaps left in the current study and offer a more comprehensive view of PP degradation. The analytical methods being already developed, any further experimental analysis will be easier to conduct and comparatively time saving.

The formulations that are recommended for further work are based on:

- **Vitamin E**

  In the further works, vitamin E is proposed to be investigated more thoroughly, especially for its interactions with the phosphite-type and thioester antioxidants (formulations P, Q and R in the Table: 7.1.). The packages also need to be tested for the phosphite replaced with the hydroxylamine (FS042) as in the formulations ‘T’, ‘V’ and ‘W’ (Table: 7.1).

- **Hindered phenols**

  The hindered phenols have also been proposed to be tested with the hydroxylamine only i.e. in absence of thioesters as in the formulation ‘S’ in the Table: 7.1. This combination will allow a

direct study of the interactions between the hindered phenols and the hydroxylamine, previously obscured by the presence of the thioesters.

In the current study, the CL and headspace emissions showed GA-80 as a stronger antioxidant than SN1010, both in solid and molten state of the polymer. The antioxidant however needs to be tested more thoroughly for its interactions with the other antioxidants, especially the thioesters and the phosphite-types antioxidants. Various important GA-80 combinations are also proposed in the Table: 7.1.

Table: 7.1. The stabilisation packages proposed for further works.

Material	P	Q	R	S	T	U	V	W
SC-110	■	■	■	■	■	■	■	■
SN1680	■	■	■					
GA-80				■		■		
Vitamin E	■	■	■		■		■	■
DSTDP		■				■	■	
SN4120			■					■
FS042				■	■	■	■	■

7.2.2. Kinetic modelling of thermo-oxidative degradation in stabilised PP

The emissions data collated during the current work can be incorporated in kinetic modelling for thermo-oxidative degradation of PP. A typical strategy that is generally followed in such work is computer-based kinetic modelling and entails:

- Establishing kinetic model from mechanistic considerations.
- Determination of the elementary rate constants for the selected mechanistic scheme, at various temperatures. This is the most challenging part of the methodology, and requires support from the kinetic data already published in scientific literature.
- Extrapolation of the elementary rate constants for various temperatures later to be used in kinetic modelling. The models thus formed can be used to predict the rate of change in the kinetic functions under a given set of experimental conditions.

Previously, the modelling has been done using ordinary differential equations solvers on MATLAB i.e. MATLAB ODE23 and ODE45 [12, 32, 71]. The same can be used for statistical analysis of the data acquired in the current study.

7.2.3. Identification of hydrocarbon isomers among the emissions

In all formations, hydrocarbons have been found as the major part of the total emissions (70-90 %). The hydrocarbons represent fragments of PP chains and can be useful for better understanding of any underlying scission patterns and their relation with degradation conditions. The resolution of the mass spectrometer (MD800) used in the current study (1 Dalton) however, was not sufficient to identify individual isomers of hydrocarbons. A high-resolution mass spectrometric analysis accompanied by ion-mobility mass spectrometry can be a useful way to identify individual hydrocarbon isomers. Provided that most of the hydrocarbons are similar among the formulations, it might not require running each sample individually hence saving time.

7.2.4. Long-term aging

The qualitative and quantitative effects of change in stabilisation packages on emissions from PP have been thoroughly investigated in the current work. The data however, applies to a relatively shorter ageing period. It requires to be extended for longer degradation period for better utility in kinetic models. Also, the formulations investigated in the current study were only singly extruded. The effect multi-passes on the polymeric emissions can be part of further work on the degradation during polymer processing. Effect of the degradation media, e.g. nitrogen, oxygen, air or vacuum, is also another important factor worth exploring.

7.2.5. Degradation and emissions during extrusion

Although an attempt of analysing and mapping the emissions from the PP at early stages of its degradation has been made, the extrusion stages of degradation have not been taken into account during the current study. Extrusion can be very important in affecting the degradation pathways that would be followed in the later stages of the polymer life-cycle. An analysis of the effluents from an extruder can provide useful information on the degradation during processing.

SPME-GC-MS methods, with some modifications in the sampling equipment, can be used to trap the PP processing effluents at various stages of extrusion, e.g. between the extrusion passes, prior and after quenching and possibly between different zones of an extruder. Studies of the relevant scope have been done previously but for polyethylene mainly, leaving a gap for PP. Such work therefore, will be an important addition to the scientific literature on PP degradation.

8. Addendum

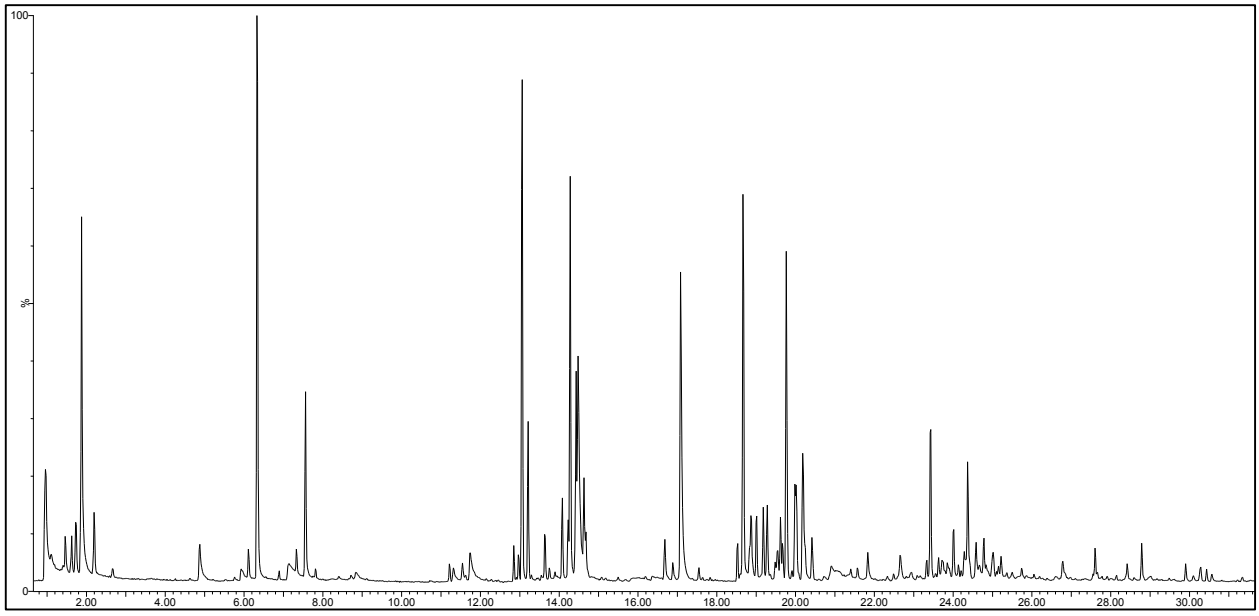


Figure: 8.1. Chromatogram of the sample D after ageing at 150°C for 20 min.

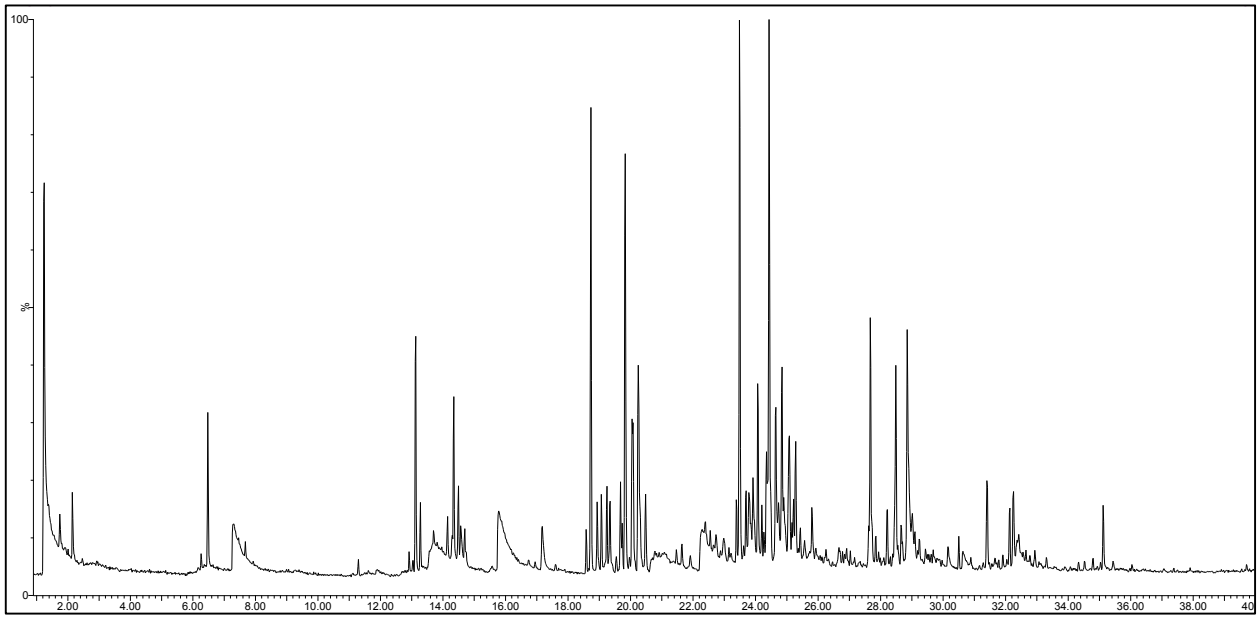


Figure: 8.2. Chromatogram of the sample D after ageing at 150°C for 60 min.

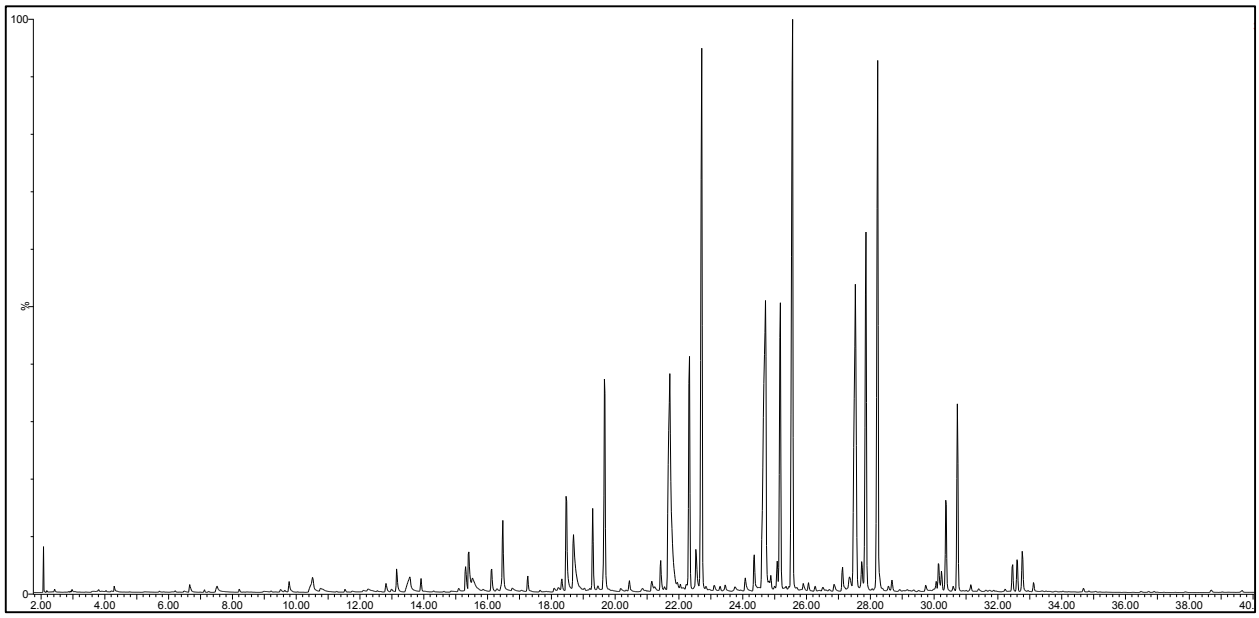


Figure: 8.3. Chromatogram of emissions from CaSt aged at 150°C for 4 hrs.

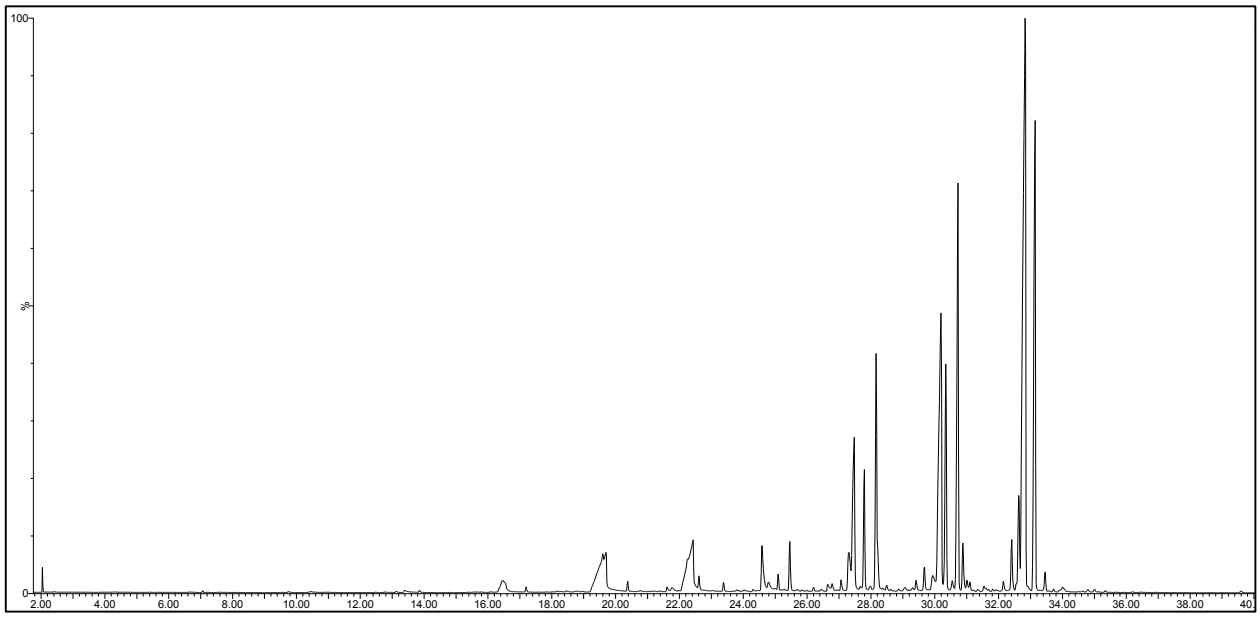


Figure: 8.4. Chromatogram of emissions from CaSt aged at 150°C for 20 hrs.

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